Health and Environmental Effects of Oil and Gas Technologies: Research Needs

A Report to the Federal Interagency Committee on the
Health and Environmental Effects of
Energy Technologies

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Health and Environmental Effects of Oil and Gas Technologies: Research Needs

A Report to the Federal Interagency Committee on the Health and Environmental Effects of Energy Technologies

Richard D. Brown
Project Manager

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The MITRE Corporation
Metrek Division
1820 Dolley Madison Boulevard
McLean, Virginia 22102

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FOREWORD

With the publication of this document, a wealth of information concerning all facets of the oil and gas industry is available under one cover. Prepared by The MITRE Corporation and subjected to review by knowledgeable individuals, this report focuses on topics of special interest to scientists, program planners, and industry officials concerned with the health and environmental issues associated with various facets of the oil and gas industry.

It is intended as a preliminary exploration, not as an assessment report. Its purpose is not to determine the precise nature or magnitude of any health or environmental problem, but instead to explore areas that may warrant further investigation.

Our understanding of the many problems discussed in this report is so limited that definitive statements cannot be made about their nature and magnitude. Where this is true, the report suggests research strategies that can increase our understanding--ultimately providing material for future assessments.

The numerous research needs identified are intentionally not ranked. Naturally they vary in significance--in the numbers of persons impacted, in the extent of environmental effects, and in the intensity of research that is required. However, a ranking would be meaningless because researchers and program managers utilize different criteria in establishing priorities. For this reason, the report provides basic information in a context that will permit individuals to set their own priorities with respect to their own research programs.

The report should be valuable to a wide range of individuals. It can be an important resource for the scientist engaged in topical research, for program planners in state and Federal agencies, and for industry, as we seek ways to make energy technologies safer for employees, the general public, and the environment.

ACKNOWLEDGMENTS

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Executive Summary

EXECUTIVE SUMMARY

This report discusses health and environmental issues associated with oil and gas technologies as they are currently perceived--both those that exist and those that are expected to emerge over the next two decades. The various sections of this report contain discussions of specific problem areas and relevant new research activities which should be pursued.

This is not an exhaustive investigation of all problem areas, but the report explores a wide range of issues to provide a comprehensive picture of existing uncertainties, trends, and other factors that should serve as the focus of future research.

The problem areas of major concern include: effects of drilling fluids, offshore accidents, refineries and worker health, soil biota and petroleum spills, indoor air pollution, information transfer, and unconventional resources. These are highlighted in the Executive Summary because they pose serious threats to human health and the environment, and because of the sparcity of accumulated knowledge related to their definition.

EFFECTS OF DRILLING FLUIDS

There are over 1,000 trade name products available for drilling fluid formulations (see Table 18 in the Offshore section for typical drilling fluid components). These are mixed as appropriate for a particular drilling activity in order to cool and lubricate the drilling bit and pipe, transport cuttings to the surface, act as a hydrostatic head against formation pressure, and to minimize corrosion.

These fluids, often termed "muds," have been identified as highly toxic to aquatic biota under laboratory conditions. It is suspected that synergistic effects among components of drilling fluids could increase toxicity. Occupational health concerns focus on dermal and inhalation exposure during formulation, handling, and disposal of the fluids. Environmental concern focuses on the toxicity of the fluids with respect to long-term exposure of biota living on the seafloor adjacent to drilling rigs and within offshore drilling fields. The possibility of food chain contamination exists.

The issue of the effects of drilling muds on human health and aquatic biota should be defined. Information gathered in this area is applicable, not only to conventional onshore and offshore drilling, but also to enhanced oil recovery and the development of unconventional resources such as heavy crude, tar sands, eastern gas

shales, western gas sands, gas-saturated brines, and gas in deep basins. This issue is discussed in both the Onshore and Offshore sections of this report.

OFFSHORE ACCIDENTS

Recently, the news media and several trade journals reported on tragic accidents associated with offshore drilling. These incidents have highlighted dangers, attracting the attention of the public and regulatory agencies to the industry's safety hazards.

One of the obstacles to assessing the extent of the problem is a lack of adequate data reporting. Currently, offshore and onshore accident data are commingled in a category termed "exploration and production." These should be segregated.

There is no comprehensive reporting program for offshore accidents. Publicly available data on offshore accidents relate only to mobile rigs and reflect a summary of press reports compiled by an industry consulting service. Offshore accident data should be divided into four categories: accidents involving tankers, fixed platforms, mobile rigs, and support vessels and structures.

REFINERIES AND WORKER HEALTH

A number of reports recently have appeared in the popular press concerning large numbers of brain tumor deaths among workers at Gulf Coast petroleum refineries and petrochemical complexes, but the significance of these findings is not clear. One conflicting study found no significant increase in the incidence of brain tumors at one of the refineries reported to have a high incidence. Similarly, other preliminary studies and analyses, most performed by affected industrial concerns, refute findings of high incidence and risk of brain tumor mortality.

The relative increased risk and any link between brain tumors and employment in the petroleum refining and petrochemical industries require further examination, although there may be no resolution and the issue may not relate to current industrial hygiene practices. This is because most deaths involve workers who began employment more than 30 years ago, before petroleum refining and work practices changed in recognition of safety and health hazards.

A recent mortality study of workers at eight refineries in the United Kingdom found no significant increased risk for brain cancer, but an above-normal incidence of malignant melanoma (skin cancer). In addition, esophageal, stomach, intestinal, and rectal cancers were found. It is possible that a new workplace hazard akin to the threat

Part 1

Introduction

posed by vinyl chloride exposure may be recognized and defined through more research. Such research is discussed in the Refinery Operations section of this report under Summary of Research Needs, Occupational Health.

SOIL BIOTA AND PETROLEUM SPILLS

To date, except for effects related to tundra and cold climates associated with the Alaskan oil pipeline, research on the ecological effects associated with oil or product spills has focused on the aquatic environment. Research is needed that focuses equally on terrestrial ecosystems as these are expected to be impacted by the numerous gathering and transmission lines to be constructed in support of new oil and gas energy sources. The soil biota of the semi-arid West and the Appalachian Basin have not been well studied with respect to oil and product spills. These areas are expected to be severely impacted by both conventional and unconventional oil and gas development. A listing of research needs related to soil biota is contained in the environment portion of Summary of Research Needs in the Transportation and Storage section.

INDOOR AIR POLLUTION

Recent research has shown that various harmful pollutants such as radon, nitrogen dioxide, and carbon monoxide have been found in the air of homes, offices, schools, and even recreational facilities. The severity of the impact of these pollutants on human health may be aggravated by government energy conservation programs which encourage the "weather-proofing" of buildings.

To date, attention on indoor radioactive emissions has focused on radon emanating from construction materials and on water supplies derived from aquifers located in sedimentary deposits rich in radioactive nuclides. Evidence suggests the possibility of an equal amount of radon released from the combustion of natural gas in gas ranges and space heaters.

Nitrogen dioxide and other emissions from the indoor combustion of oil and gas also may compound the problems with and reactions of indoor air pollutants. Nitrogen dioxide levels have been found to be significantly higher (in some cases seven times higher) in homes with gas stoves than in homes with electric stoves. Gas appliances also have been cited as significant sources of carbon monoxide. However, research has focused on air pollutants associated with the infiltration of automotive exhausts and on volatile solvents.

The nature, magnitude, and role of radioactive and chemical emissions from the indoor, energy-related use of oil and natural gas should be determined. Research in this area should be integrated with a comprehensive research program that addresses all facets of indoor air pollution.

INFORMATION TRANSFER

The techniques proposed for recovering oil from U.S. tar sands are also applied to recovery of deep light oils and heavy oils, and enhanced recovery of oil shale by in situ techniques. Some heavy oils are produced in California and Texas by thermal methods (and are included in conventional oil reserve estimates). Gas from geopressured brines, eastern shales, western tight sands, and deep basins is expected to be extracted through the application of fracturing and the use of drilling muds--methods that are also employed to recover the resources named above.

These resources are classified by various Federal agencies under different programs, depending upon the agency's convenience and statutory mandates, pricing categories for the resource, and definition of conventional versus unconventional resources. As an example, research in support of heavy oil may be categorized as conventional crude oil research by one agency and as support of synthetic fuels development by another (the Energy Security Act classifies undeveloped heavy crude as a synthetic fuel). As a result, many duplicative development and research strategies are taking place. Often, identical generic and region-specific health and environmental research activities can apply to several technologies. An information transfer strategy is needed which will enable relevant generic, regional, and process-specific research to be brought to bear on solving similar oil and gas health and environmental effects problems.

INTRODUCTION

The oil and gas industry is entering a new era in terms of the nature and diversity of resources and requirements of transportation and supply. The petroleum industry is directing more of its profits than ever before into the search for new energy supplies. In 1980, the industry spent more than \$50 billion on exploration and production inside the U.S.--26 percent more than the \$40 billion spent in 1979. About 60,000 wells were completed in 1980 (about 35 percent more than in 1979)--breaking the 1956 record of 58,160.

With the additional emphasis on the extraction of oil and gas from unconventional sources and on the development of petroleum substitutes from coal and oil shale, the entire oil and gas industry is likely to change. Now dependent upon imported gas and petroleum and on conventional domestic reserves, it is likely to become a diverse and complex industry within the next decade. The traditional association of the industry with fossil fuels (oil and gas related to biological decomposition and mineralization over the geologic time span) will be enlarged to include interaction with geothermal resources (gas saturated brines), synthetic fuels (in situ recovery of oil from tar sands and heavy crude), energy conservation (waste oil recovery), and agriculture (oil and gas from biomass).

The character of the industry, both at present and in the future, is the subject of this report (Figure 1). Various facets of the industry are addressed in terms of potential health and environmental issues. The technology and research activities which should be undertaken to understand the issues are identified and a few broad research issues are discussed in the last chapter.

The changing character of the oil and gas industry creates the potential for new impacts on human health and the environment. Consequently, changes in the industry are briefly discussed below.

CONVENTIONAL ONSHORE AND OFFSHORE DEVELOPMENT

The recent increases in energy prices have provided an incentive for accelerated oil and gas development. In December 1980 the number of U.S. rotary drilling rigs exploring for new oil and gas reached 3,200--the highest number in 23 years. In the last year alone, the amount of drilling activity in the Permian Basin of Texas increased by 50 percent. This new drilling follows a decade of declining exploration and production (Newsweek 1980). Accelerated oil and gas development is expected to continue and even markedly increase as the new administration focuses on increased production of domestic oil and gas reserves.

Alternative Sources of Oil and Gas Extraneous to the Conventional Oil and Gas Industry Sequence

1. Imported Natural Gas	8. SNG from Methanol, Napththa, etc.
2. Imported LNG	9. Gas from Oil Shale
3. Imported Crude Oil	10. Oil from Oil Shale
4. Imported Oil Products	11. Gas from Solid Organic Wastes and Biomass
5. Natural Gas Liquids from Gas	12. Oil from Biomass
6. Oil from Coal	13. Waste Oil Recycling
7. Gas from Coal	14. Gasohol

^aStorage is an integral part of each component.

FIGURE 1
COMPONENTS OF THE OIL AND GAS ENERGY SEQUENCE

Conventional development of eastern U.S. gas reserves focuses on tapping previously unexplored strata. One well recently tested at 1.6 million cubic feet a day (exceptional for Ohio). In central Pennsylvania, an Amoco well tested at 20 million cubic feet a day (average daily consumption of natural gas in 1978 was about 52 billion cubic feet a day) from a previously unexplored basin. In West Virginia, a well drilled into a shallow formation near Clarksburg tested at 7.5 million cubic feet a day. New findings related to the formation of the Appalachian Mountains suggest the possible existence of large amounts of untapped oil and gas (Hodgson 1978; Technology Forecasts 1979).

Offshore oil and gas development is rapidly accelerating and undergoing dramatic changes. While rotary drilling began around 1900, offshore drilling started as recently as 1947. Drilling from floating platforms began in 1953 and the use of subsea wells began in 1962. In 1970, drilling in 1,300 feet of water was accomplished, followed by the development of dynamically stationed drillships in 1971. In 1980, 500 mobile rigs were operating. Exploration drilling has occurred in 5,000-foot depths. Some drilling units now are equipped to drill and produce oil in 6,000 feet of water, and equipment is available for drilling and well completion in 8,000 feet of water.

Experience with deep ocean operations such as dredging seafloor muds at 8,000 feet, deep ocean mining in 16,000 feet of water, and ocean floor coring at 18,000 feet opens new horizons for offshore oil and gas development beyond the continental slope. The U.S. Geological Survey has found evidence from seismic data of a large carbonate reef extending along the entire U.S. East Coast and possibly around the Gulf of Mexico. This reef, underlying the continental slope at a water depth of 6,000 feet, is overlain by about 6,000 feet of clastic sediments which may be porous and permeable to provide sizable hydrocarbon reserves (King 1980; Hammett 1980).

REFINERY OPERATIONS

Refinery operations traditionally have evolved slowly to meet new process demands. Rather than focusing on the construction of new plants, most refineries undergo "modernization," in which facilities are upgraded in certain ways to increase capacity and efficiency, to meet new pollution control requirements, and to produce a new product.

Refineries are facing new needs for expansion brought about, in part, by increased emphasis on the conventional development of domestic oil reserves. Some refineries designed to process imported

Arabian light crudes may need to be altered in order to process certain heavier and high sulfur U.S. crudes. The new impact of synthetic liquids produced from coal and oil shale will require substantial changes in capacity and unit processes.

Production efficiency is expected to be improved as a major step toward reducing U.S. dependence on imported crude oil. Refineries now consume 1/10th of the oil they process (Maier et al. 1979). An example of an efficiency improvement was announced recently by Ashland Oil, Inc., which has developed a process to refine 25 percent more gasoline from a barrel of crude oil than is now possible. This breakthrough, requiring a \$70 million refinery addition in Kentucky, will use a reduced conversion process, which allows the production of more gasoline from the heavy, sludge-like portion of crude that normally has been sold as a low-priced boiler fuel or made into asphalt (O'Toole 1980).

LIQUEFIED ENERGY GASES

Incentives for developing liquefied energy gases include: the recent uncertain availability of existing domestic gas supplies, questions regarding the timing of demand and exploitation of new domestic supplies, and potential interruptions in the supply of imported LNG and natural gas. Liquefied energy gases used for peak-shaving in a single 24-hour period during the 1980 winter season came from a variety of sources, including 57 billion cubic feet from underground gas storage, 5 from propane-air plants, and 9 from LNG peak-shaving and satellite plants. This represented 83 to 89 percent of the 1980 winter, peak-day sendout considered the maximum that would be required (Hale 1980). Clearly, liquefied energy gases, particularly LNG, play an important role in supplying gas for residential and industrial use. More storage units will be required as new conventional and unconventional sources of natural gas are developed.

TRANSPORTATION AND STORAGE

Transportation and storage networks are indispensable, forming a link between production, refinement, and use of oil and gas resources. With expansion of the oil and gas industry, geographic relationships between sites of supply and consumption will change dramatically. The development of unconventional sources of oil and gas, new conventional sources in the eastern Appalachian Basin and the western Rocky Mountain Overthrust Belt, and synthetic fuels will require thousands of miles of new gathering and transmission lines. Many of these will be situated in relatively inaccessible areas and will be accompanied by extensive road construction.

END USE

Even with economic recession, the demand for oil in the industrialized world can likely rise by 300,000 to 500,000 barrels per day, and increased requirements of the developing world will add a daily average of about 100,000 barrels to this total (Energy Insider 1980). Oil and gas are the fossil fuels of choice because of the have advantage over coal in terms of ease of handling, clean fuel attributes, and potential for petrochemical feedstocks. The demand for oil and gas will continue to grow. The role synthetic fuels and unconventional resources will play in filling this demand will depend upon future political and economic forces and decisions.

UNCONVENTIONAL RESOURCES

In the last 100 years, over 450 barrels of oil have been discovered in the U.S. However, only about 115 billion barrels have been produced. Current advances in conventional drilling technology can allow only for the production of another 30 billion barrels from these fields, leaving about 305 billion barrels. Another 26 billion barrels of oil are contained within Utah's tar sands; 30 billion barrels of heavy, viscous barrels are located in California; and billions more are in shallow diatomite formations and tar sands elsewhere. Much of this oil is recoverable by the new techniques of oil mining and in situ extraction.

With respect to natural gas, only a small increase in production from new sources can more than quadruple the current estimate of recoverable reserves. These new sources include methane-saturated brines, eastern gas shales, western gas sands, methane from coal seams and mines, methane hydrates, gas in deep basins, and gas from biomass. Moderate gas recovery from these new reserves could extend the current 10-year supply of conventional natural gas (from conventional sources at current consumption rates) to over 100 years.

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Part 2

Onshore Development

ONSHORE SUMMARY

This section points to health research needs associated with onshore oil and gas development, with emphasis on the need for improved collection of health effects data, information on occupational health effects associated with the use of drilling fluids and chemicals and gases utilized in enhanced recovery methods, and the need for regional health assessments of the cumulative impact of airborne and waterborne contaminants associated with oil and gas production.

Research is also needed on the environmental effects associated with onshore oil and gas development. Better methods should be developed to track the movement of pollutants through groundwater systems and information is needed on the transformation and fate of surfactants, solvents, and other groundwater contaminants related to oil and gas recovery.

Specific research needs in the above problem areas can be found within the Summary of Research Needs sections. These summary sections follow related discussions of health and environmental problems. Discussion of the effects of oil spills on aquatic or terrestrial biota is presented within the Transportation and Storage section of this report.

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ONSHORE OIL AND GAS PRODUCTION

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ONSHORE OIL AND GAS PRODUCTION

TECHNOLOGY DESCRIPTION

Oil Extraction

Crude oil exists in and is extracted from underground rock formations, termed reservoirs. These reservoirs may be composed of sandstone, limestone, or dolomite structures (American Petroleum Institute 1976). Within an oil reservoir, there may be varying amounts and kinds of naturally occurring energy resources in addition to crude oil or natural gas. These are (National Petroleum Council 1976; American Petroleum Institute 1976):

- o Dissolved gases within the crude oil,
- o Dissolved gases within associated saltwater deposits that may coexist with the crude oil,
- o Free (non-dissolved) gases that occur with the crude oil, and
- o Free deposits of water (usually brine) associated with crude oil, in which gas may or may not be dissolved.

Recovering the oil and gas from these reservoirs is a multi-step process that begins with exploratory surveys, before proceeding to primary production, and then often to the use of enhanced recovery techniques.

Exploration and Site Preparation

Exploratory surveys to locate likely petroleum and gas bearing strata are the first step in oil and gas production. Surface surveying methods involve using aerial and satellite photography in conjunction with on-site studies of the surface topography and geology. Subsurface analytical methods may include using gravimetric, magnetic, and seismic instruments. Seismic readings are obtained by recording shock waves that penetrate the earth's crust (Wilkins 1977). Shock waves can be generated by explosive charges planted on or in the earth's surface (Coffeen 1978). Such explosives have a limited potential for polluting shallow streams when the seismic shot is not properly cased (Wilkins 1977).

If instrument readings indicate a potential petroleum deposit, site preparation and preliminary core drilling may begin. This phase of preliminary operations involves using various types of land clearing and drilling equipment which can greatly modify the

vegetation and soil surface of the affected area. In addition, the environment may be impacted by noise, dust, and combustion-related emissions from the equipment.

Perhaps the greatest potential danger associated with site preparation involves the initial drilling procedure itself. A "blow-out" (Britt et al. 1976), or uncontrolled flow of crude petroleum and associated components, can occur when an oil or gas formation is breached. Blowouts can spread large amounts of crude petroleum containing many organics that are potentially toxic and not readily degradable, choking vegetation, destroying animal habitats, and covering workers. In addition to direct land and water pollution, fire associated with such blowouts results in release of gaseous and particulate air pollutants (e.g., hydrocarbons, nitrogen oxides, sulfur oxides, and carbon monoxide). These may pose additional safety hazards (Britt et al. 1976). Special drilling fluids and mechanical valves are generally employed to help prevent blowouts. Another hazard associated with drilling is land subsidence, which can occur accidentally in normal oil drilling and extraction procedures.

Primary Production

The utilization of naturally occurring gases and water to initiate oil movement from the reservoir to the earth's surface is termed primary production. After exploratory and test procedures indicate the existence of an oil reservoir, the next step is primary production drilling, which requires the use of drilling equipment and complex chemical fluids. Modern methods of primary production primarily utilize rotary drilling. In this form of extraction, a rotating drill bit, connected by many hollow lengths of pipe termed "the drill string," chips and gouges its way through soil and rock strata. The drill and its associated drill string are encased within a drill pipe. The hole (well bore) created by the rotary drill is constantly kept full of a chemical fluid called "drilling mud," composed of mixtures of clay, water, and various chemical compounds. (Sometimes compressed air is used in place of mud.) Mud is sent down the well bore through the hollow pipes forming the drill string and then is recirculated back to the surface through the space between the drill string and the large-diameter pipes forming the casing string which line the borehole. At the surface, rock cuttings and fines from the drilling are separated from the mud. This takes place through use of shakers, desanders, and desilters (Wilkins 1977). The purified mud can then be recycled. If the mud is too contaminated for cleaning, it may be disposed of in waste pits, along with the rock cuttings and other waste products (Wilkins 1977).

The use of drilling mud is critical during the initial extraction stages and serves some of the following functions (Richards 1979):

- o Lubricating the drill string,
- o Cooling the rotary drill bit,
- o Carrying the rock cuttings/fines from the well bore to the surface,
- o Preventing parts of the penetrated formation from entering the well bore,
- o Inhibiting the entrance of undesirable formation fluids into the well bore, and
- o Controlling excessive pressure in the well bore to prevent blowouts.

After the oil bearing stratum is reached, there is a shift of emphasis from drilling to the establishment of a production well (termed well completion). The two basic methods of well completion are termed "open hole" and "perforated completion" (Allen and Roberts 1978). Both of these procedures involve cementing a string of connected pipes (casings) into the drilled hole. In open hole completion, the casing sits on top of the producing strata. In perforated completion, once the casing is in the producing level, steel bullets or shaped charges penetrate the casing and the cement in which it is set (Wilkins 1977). Holes are blown into the strata so that petroleum may seep into the casing. Ninety-five percent of all well completions are currently accomplished by the perforation method (Wilkins 1977). Regardless of which well completion method is utilized, a small production tube (or tubes) is installed within the perforated casing. It is through this production tube that the crude oil is brought to the surface.

Upon reaching the surface, crude oil must be separated from other components with which it is associated. The two major components are brine (water containing, or saturated with sodium chloride and other salts) and natural gas. As a primary contaminant, brine must be removed on site before the crude petroleum is sent to the refinery for further processing (Wilkins 1977).

Mixtures of oil and water (usually brine) often occur as emulsions either as water in oil or oil in water (Case 1970). The latter indicates a declining production situation in which the bulk (80 to 90 percent) of the fluid leaving the oil formation is water with

colloidal oil droplets (Case 1970). The former is reflective of more desirable production situations in which water is not the primary component of the emulsion. In addition to emulsions, brine may also be associated with crude oil as free water. In this situation, the water is gravimetrically separated from the oil. The water and oil mixture then enters large tanks in which baffles are inserted to minimize turbulence and to enhance the water and oil separation (Wilkins 1977). This procedure is known as free water knock-out.

Water and oil emulsions require more elaborate treatment techniques to achieve separation of the two components. Heaters and electric dehydrators are used to physically separate the oil from the brine. Chemicals may also be added to destabilize emulsions. Once the mixture is broken into two separate phases, gravitational settling can occur and water can be drawn off and disposed of. The resulting crude oil is then sent to the refinery.

A considerable amount of brine may remain after crude oil separation. It is estimated that two to three cubic meters of brine are produced for every cubic meter of oil (Wilkins 1977). The majority (72 percent) of this brine is disposed of in underground formations or used for injection purposes during secondary recovery (Wilkins 1977). The remainder may be disposed of in non-potable water supplies, or in approved disposal areas, unlined pits, or rivers (Wilkins 1977).

In addition to brine, other by-products and emissions also may be produced in significant quantities. It has been estimated that 33 metric tons per day of hydrocarbon compounds can be collected in wastewater separators alone (Wilkins 1977). Some desirable components within crude oil such as natural gas are extracted in the field. Hydrogen sulfide may be emitted from crude oil and brines where it has been held in solution under pressure.

Enhanced Oil Recovery

Enhanced oil recovery is the use of any technique to extract more oil than that which is obtained through primary production (Schumacher 1978). The various techniques are divided into two categories, secondary and tertiary methods.

Secondary Recovery Methods

Secondary recovery techniques include the injection under pressure of either treated water or immiscible (natural) gas into an oil formation to increase the petroleum flow. The injection of water, termed waterflooding, is by far the most important of these two techniques (National Petroleum Council 1976). It is estimated that, by

1973, 1/2 of domestic oil was obtained from reservoirs tapped either in part or entirely through water flooding (Schumacher 1978). The use of natural gas injection to maintain reservoir pressure and augment declining well production has been steadily decreasing. One of the primary reasons for this is that waterflooding is far more efficient than gas for displacing oil (Office of Technology Assessment 1978; Schumacher 1978). The increasing value and price obtained for natural gas in the commercial market is another factor limiting its use for secondary recovery.

Waterflood operations utilize two types of wells: production and injection wells. Treated water is pumped into the injection wells and down to the petroleum containing formation. The injected water forces trapped petroleum held within the formation into the production wells where water pressure forces the oil to the surface of the reservoir. The production fluid reaching the surface is a mixture of oil and injected water. This mixture is then separated using the same procedures described under primary production.

Common sources of injection water (usually brine) are: (1) water separated from oil, (2) brine or fresh water obtained from near the oil formation, (3) surface water (rivers, lakes, oceans), and (4) alluvial wells (Patton 1977). Whatever the source, the injected water usually requires treatment with various chemicals to prevent scale formation, inhibit corrosion, and prevent the growth of microorganisms. The nature and extent of the chemicals added to the injection water are of environmental importance, since surface and sub-surface contamination can result from spillage or seepage of either the mixed production fluid (treated water and oil) or the separated brine which requires disposal.

Brine and its associated components are often disposed of in brine disposal wells. These are frequently old, depleted oil wells converted for other uses (Schumacher 1978). Usually, when the waste stream is injected into these wells, pressure is employed. This may cause fractures which can then result in seepage into freshwater aquifers.

Tertiary Recovery Methods

There are four major tertiary recovery techniques:

- o Hydrocarbon-miscible flooding,
- o CO₂-miscible flooding,
- o Micellar and polymer flooding, and
- o Steam and in situ combustion.

These methods fall into two basic classes: the first three reduce surface tension between oil and the driving fluid, while the last employs heat to reduce the viscosity of the oil (Schumacher 1978).

- o Hydrocarbon-miscible flooding methods.

There are three basic extraction techniques that involve the use of gaseous hydrocarbons to move reservoir oil to the surface. The high-pressure gas technique uses gaseous hydrocarbons as the driving fluid under high pressure (3,000 psi) and is applicable to reservoirs that contain low viscosity oil. A prerequisite for this process is that the reservoir be able to sustain the use of such high pressures (Schumacher 1978). This method makes use of the pressure to transfer the lighter hydrocarbon gases out of the oil to form a leading gas front. The initial gas front then evaporates more of the same light hydrocarbons from the remaining oil, thus forming a self-sustaining, miscible slug.

The enriched gas technique differs from the former method in that a miscible front is obtained by directly injecting gaseous hydrocarbons into the oil reservoir, rather than by depending on high pressure to extract gas entrained within the reservoir oil.

The third hydrocarbon flooding method, the miscible (LPG) slug process, involves injecting hydrocarbons of intermediate molecular weights into the reservoir. After this, gas injection may be employed (Schumacher 1978).

The use of hydrocarbon-miscible techniques is quite limited due to the high pressures required and the environmental hazards associated with blowing through the overlying structures. In addition, these methods suffer from a poor mobility ratio (Schumacher 1978). Finally, and most important, the hydrocarbons being used as driving fluids may have a greater value in the marketplace (National Petroleum Council 1976).

- o Carbon dioxide-miscible flooding.

This method is analogous to that of the high pressure (hydrocarbon) gas technique previously described. CO₂ is used to displace the gaseous hydrocarbons from the reservoir oil. These displaced components form the miscible zone. Besides the availability of CO₂, this method has other advantages. A much larger group of hydrocarbon components is vaporized from the oil than with the hydrocarbon technique.

Also, this method may be employed in reservoirs under lower pressures than are required for some of the hydrocarbon recovery techniques (Rahme 1978).

- o Water-miscible flooding methods.

These methods include both micellar (surfactant) and polymer flooding techniques. In micellar flooding, a specified slug of surfactant solution, varying from 5 to 10 percent of the reservoir volume, is injected into the oil formation (Rahme 1978). This solution causes the formation of micelles or microemulsions (Schumacher 1978). The types of surfactants used include petroleum sulfonates, various hydrocarbons, alcohols, and inorganic salts (National Petroleum Council 1976). Whatever the nature of the detergent-like surfactants, they act to reduce the amount of oil-water tension and to solubilize and emulsify the oil, so that it may be moved more readily from the formation.

Polymer flooding involves the use of high-molecular-weight compounds added to the water that is injected into the oil reservoir. This method, in effect, is an augmented waterflooding technique. The polymers serve to increase the viscosity of the water being injected, thus enhancing the mobility ratio of the waterflood. In addition, they also decrease the permeability of the formation to the water being injected (National Petroleum Council 1976). The polymers used are generally either polyacrylamides or polysaccharides.

Due to the diverse chemicals employed in both surfactant and polymer flooding, these recovery methods may present a potential for environmental and health hazards, either through direct use, as a result of an accident, or when they are disposed of.

- o Steam and in situ combustion techniques.

Steam and in situ combustion techniques are thermal methods which generate and apply heat to viscous crude oils to reduce the viscosity of oil, thus allowing it to flow more easily (Schumacher 1978). The use of steam injection is the most technologically advanced and widely used of any of the enhanced recovery methods (Office of Technology Assessment 1978).

There are two basic types of steam technologies: cyclic steam injection and steam drive. The former method is sometimes characterized as the "huff" (injection phase) and

"puff" (production phase) technique. It uses the same well both for injecting the steam and obtaining the produced oil. Initially, high pressure steam is injected into the well for a specified period of time ranging from days to weeks, then the injection phase (huff) is stopped. The well is capped while the reservoir soaks up the injected steam. When the well is later reopened, the condensed water within the pressurized reservoir is converted back to steam. This occurs as a result of flashing and of a decrease in well pressure upon reopening (puff).

An alternative method involves the use of steam drives and a system of separate injection and production wells. Steam is continuously pumped down the injection wells. As the steam condenses in the reservoir, a hot water zone is formed which pushes a mixed zone of oil and water toward the production well.

As with waterflooding and micellar-polymer flooding, there are potential environmental consequences with the steam technologies. Producing high pressure steam and pumping it down to the reservoir requires energy. The steam generators used in these thermal processes consume large amounts of oil. As a result, significant amounts of combustion products may be vented to the atmosphere. With steam generators it has been estimated that 40 lbs of hydrocarbons, 4,000 lbs of sulfur oxides, 800 lbs of nitrogen oxides, and 280 lbs of particulate matter could be emitted for every 1,000 barrels of oil produced (National Petroleum Council 1976). It is assumed that, of all the enhanced recovery techniques, the ones most likely to cause air quality impacts are those involving thermal processes.

The in situ combustion technique also makes use of heat to reduce oil viscosity. In this method, heat is produced within the reservoir itself. Air is injected into the formation and part of the crude oil is ignited and burned in place. This reduces the viscosity of the remaining oil and the combined effect of vaporized oil, steam, and gas pushes the bulk of the oil to the surface. As with the steam methods, air quality may be compromised. Combustion products may be vented through surface fissures or cracks. In addition, various chemical pollutants may remain within the reservoir as a result of in situ burning. These may contaminate aquifers if the burn site is flooded. Measurement of some of the gaseous compounds emitted from in situ projects has shown that carbon dioxide, carbon monoxide, sulfur and nitrogen oxides, oxygen, and various hydrocarbons were produced.

Natural Gas Extraction

Natural gas occurs in four types of reservoir situations: (1) dissolved gas within crude oil deposits; (2) associated (free) gas occurring with crude oil (e.g., in gas caps); (3) non-associated gas; and (4) gas dissolved within brines.

Natural gas is a desirable energy resource sometimes found associated with reservoirs of crude oil. It is removed from the petroleum at the production site before being sent for further processing. The gas is dissolved within oil, so the extraction process is basically one of using separators to remove the gas. There are two types of separators: two-phase units that separate oil from gas, and three-phase units that separate oil, gas, and water. The configuration of the separators may be vertical, horizontal, or spherical, depending on the gas-to-oil ratio (Wilkins 1977).

Waste streams result from oil and gas separation. This may be especially true where relatively small amounts of gas are separated from crude or in remote areas where economic incentives do not justify further gas processing steps. In this context, it has been estimated that 50 billion cubic feet of natural gas are lost each year to the atmosphere through venting, flaring (burning), and other fugitive losses (Wilkins 1977). In addition to these hydrocarbon emissions, there may be considerable amounts of sulfur-containing compounds associated with particular types of gas.

Whether dissolved in oil or found by itself, natural gas may contain hydrogen sulfide (H_2S), a hazardous substance which must be removed before further processing. The removal of hydrogen sulfide usually is carried out by passing the natural gas-hydrogen sulfide mixture through a monoethanolamine solution. This absorbs the H_2S . Subsequently the monoethanolamine is stripped of the H_2S and recycled. The free H_2S can then be burned or sent to a sulfur recovery plant. If it is burned, there may be considerable amounts of SO_2 released to the atmosphere (Leggett and Williams 1979).

In addition to H_2S removal, all natural gas having a water content greater than five to seven lbs per million cubic feet must have water eliminated before further processing. If this is not carried out, gas hydrates will form. Gas dehydration is usually accomplished by glycol absorption. Either di- or tri-ethylene glycol is used to absorb water from the gas and is then recycled with the free water vapor being vented to the atmosphere (Leggett and Williams 1979).

Enhanced Gas Recovery

Enhanced gas production (gas stimulation) methods are now commonly used, especially in gas formation. These methods include hydraulic fracturing techniques, chemical explosive fracturing, and directionally controlled drilling. It should be emphasized that fracturing techniques are not unique to enhanced gas recovery, but also are used to stimulate oil production (Allen and Roberts 1978). All fracturing techniques involve increasing the reservoir area from which gas may be obtained and increasing the gas flow by breaking or fracturing the reservoir formation.

Hydraulic fracturing is a process whereby large quantities of a fluid are pumped under pressure into a gas formation. This is exemplified in the single-well technique, with which a fluid injected through the wellbore initiates a fracture. Along with the fluid, a coarse sand or other material is injected to keep the fractures open for gas flow after fluid injection is stopped. The produced gas then flows up the same well bore (U.S. Department of Energy 1979). This type of fracturing has a special use in "tight" gas-bearing formations, which include certain sand and shale formations. For example, in Amoco's Wattenburg Field in Colorado, hydraulic fracturing is used to increase production from certain tight bearing marine sands (Hanson et al. 1978). Various fluids, in addition to water, may be used for fracture induction. For example, foam, cryogenics (low temperature liquids that expand), and gelled water have been utilized in some tight eastern sandstone and Devonian shale formations (Forrest and McKetta 1978).

In addition to hydraulic fracturing, explosive fracturing may also be utilized. There are two basic explosive techniques: (1) borehole shooting, which consists of lowering an explosive down the drilled hole and then opening a hole by detonation; and (2) pumping an explosive liquid slurry into the formation itself and then detonating the mixture (U.S. Department of Energy 1979).

Directionally controlled drilling is still another approach that is being investigated as an enhanced gas recovery technique. This takes advantage of the natural fractures existing in a formation and orients the direction of the drilling so the fractures will be intersected by the drill. This technique is used particularly for the extraction of gas from coal seams.

Whatever type of enhanced recovery technique is used, when the gas reaches the surface it will be separated from impurities such as water vapor and hydrogen sulfide and then will be sent for further processing, if needed. Hydrogen sulfide is a particular problem in the exploitation of the western overthrust belt and perhaps in deep

basins. In certain deep basins, such as the Anadarko surrounding the Oklahoma panhandle, high pressures (i.e., 20,000 psi) can cause casing failures.

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HEALTH EFFECTS OF ONSHORE DEVELOPMENT

The potential impact of oil and gas production on occupational and public health is multifaceted both in scope and in the number of problems encountered. These problems may be specific to one technology or they may be present among a large number of technologies, but differ in the degree of associated impacts. This section presents an overview of potential health effects resulting from the production of oil and gas and offers directions for future research.

Occupational Health Hazards

Drilling

The major emphasis in this section is on reviewing the effects of exposure to materials used in production, the produced fluids, and their associated components. Where applicable, problems unique to specific technologies are addressed.

During exploration and drilling, health impairment is likely to be in the form of mechanical injury as a result of accidents. Workers are exposed to hazardous situations resulting from maintenance activities, equipment failure, oil rig set-up, and rig dismantling activities. In addition, high risk may be involved in geophysical or seismographic exploration and testing, which often require extensive aerial surveys and the use of explosives to determine geological formation profiles.

The actual number of field accidents reported in 1978 that involved both injury and death may be divided into two categories: exploration/production and drilling. Data from 109 oil and gas companies (American Petroleum Institute 1979a) indicated that, of 72,749 employees in exploration and production, 2,758 (4 percent) were injured and 21 were killed. In drilling, there were 2,947 workers and 809 (3 percent) were injured, while 1 was killed. In the former category, the varied causes of death included: electrocutions, drownings, fatal falls, escaping gas, and helicopter or aircraft crashes (American Petroleum Institute 1979b).

These data reflect both onshore and offshore sites. There is no available breakdown of the relative number of deaths and types of injuries associated with either onshore or offshore production technologies. There is an apparent need to assess the relative hazards associated with each type of production technology and to identify potential hazards that may be unique to different technologies. An obvious, but important, point of emphasis is that even the same extraction technology may present quite different degrees of danger depending on its location. For example, potential disposal and

exposure hazards associated with production or waste products on the limited area of an offshore platform may be quite different from those on an onshore site--especially during emergency procedures that could necessitate rapid evacuation measures. In addition, climate affects the types of clothing workers may wear and the protective measures they use.

Petroleum Extraction

During the initial (primary) extraction of oil, large amounts of drilling muds are employed. It is estimated that a well 8,500 to 11,500 feet (2,600 to 3,500 meters) deep requires 1,200 to 2,500 barrels of mud (Wilkins 1977). There are two basic types of drilling muds: water-based and oil-based. These terms refer to the liquid phase of the mud to which various chemical compounds are added (U.S. Environmental Protection Agency 1976). Onshore drilling usually employs freshwater muds, although saltwater- or oil-based muds may be employed for drilling through salt formations.

Drilling muds vary greatly with regard to their formulation. However, some of the more commonly used constituents in freshwater muds are: lignosulfonates, acrylonitriles, caustic lignin and tannin, emulsified asphalt, sodium polyacrylate, carboxymethyl-cellulose, and formaldehyde (Wilkins 1977). Several of these compounds have been shown to be carcinogenic in animals, including asphalt, tannins, formaldehyde, and acrylonitrile monomer. Although not generally used for onshore drilling operations, the oil-based muds may contain various mixtures of oxidized asphalt, organic acids, alkalis, stabilizing agents, and diesel oil (U.S. Environmental Protection Agency 1976).

Due to their varied and unknown compositions, these mud formulations may introduce large amounts of potentially hazardous compounds into the work site. Workers and those in the immediate vicinity may be exposed to hazardous constituents through a number of routes--dermal exposure, percutaneous absorption, inhalation of volatile components and aerosols, and ingestion. In addition, workers' families may be exposed to compounds on clothing and the workers' personal effects, such as automobiles.

Information on the contents and toxicity of the various mud formulations is not readily available. Studies are needed to document the extent of worker exposures to drilling muds and assess potential health risks associated with occupational exposures to the various kinds of muds under diverse drilling operations.*

*For information on the offshore use and effects of drilling muds, the reader is referred to the Offshore section of this report. A summary of bioassay information and ecological effects is provided.

The drilling muds often contain formation cuttings that must be separated when they reach the surface. Drilling a 15,000-foot hole 8-1/2 inches in diameter produces 1,059 barrels of cuttings (Wilkins 1977). Often the mixture of cuttings and drilling mud is further contaminated with associated crude oil. The cuttings may contain hazardous materials, such as heavy metals, which may affect the environment and health.

In conjunction with drilling, a direct threat to the health and safety of workers may arise as a result of well blowouts, especially in the drilling of deep wells. In addition to causing direct injury, blowouts also cause direct cutaneous, aerosol, and vapor exposures to crude petroleum with its associated organics, poisonous gases (such as hydrogen sulfide), and drilling mud constituents. If fire is associated with such an event, carbon monoxide, oxides of sulfur and nitrogen, and organic particulate matter also would be emitted (Lawrence 1976).

In other methods of oil extraction, such as waterflooding, potential health hazards may involve exposure to chemical constituents of the treated injection water as well as mixed production fluids. An important point of emphasis with respect to both secondary (waterflooding) and tertiary techniques is that the chemicals which become mixed with crude oil are often removed when the oil is recovered, which concentrates them and associated compounds (Antizzo and Lawrence 1976). The injection water used in a waterflood project usually requires chemical treatment prior to use; chemicals that may be employed include bactericides, scale inhibitors, anti-corrosives, anti-precipitants, and sequestering agents (Patton 1977).

A recent publication reviewed some of the toxicological properties and associated research needs for compounds used in enhanced oil recovery (Silvestro and Desmarais 1980). Some of these compounds are classed by use in Table 1. Toxicity values for many enhanced oil recovery compounds are presented in Table 2. Some generic and specific potential hazards are discussed below.

Surfactants used may pose significant occupational health hazards. Most surfactants act as irritants on contact with the skin and mucous membranes and when inhaled. Petroleum and aryl sulfonates have demonstrated carcinogenic activity in animals and yield sulfur oxides when heated. Sulfonation is generally performed on site, suggesting that high exposure potentials may occur. Synergistic actions and solubilization of other hazardous agents may compound the adverse effects of surfactants in oil recovery operations.

TABLE 1

SOME CHEMICAL AGENTS USED IN OIL RECOVERY

Mobility Control Agents

Polyacrylamides
Xanthan gums
Carboxymethylcellulose
Hydroxyethylcellulose
Polyethylene glycol monobutyl ether
Polyethylene oxide

Cosurfactants

1-hexanol
2-hexanol
1-octanol
2-octanol
n-butanol (and tert-, sec-, and iso-isomers)
Cyclohexanol
Polyethoxyalkylphenol

Biocides, Chelating Agents, Oxygen Scavengers

Quaternary ammonium chloride
2,4,5-trichlorophenol
Pentachlorophenol
Phenol
2,2-dibromo-3-nitrilopropionamide
Copper sulfate
Glutaraldehyde
Formaldehyde
Sodium hypochlorite
Acrolein
EDTA
1,6-hexandeamine

Surfactants

Alky aryl sulfonates
e.g., Alkyl benzene sulfonate
Octadecyltoluene sulfonate
Tridecyl benzyl sulfonate
Decyl benzyl sulfonate
Alkyl naphthenic sulfonates
Petroleum sulfonates

TABLE 1 (Concluded)

Alkaline Flooding Agents, Preflush Agents,
Thermal Enhancers

Sodium nitrate
Sodium hydroxide
Sodium orthosilicate
Sodium carbonate
Sodium borate
Sodium hydrosulfite
Sodium bisulfite
Sodium sulfate
Hydrazine
Quinoline
Toluene
Xylidine
Aniline

TABLE 2

GENERAL TOXICITY DATA FOR CHEMICALS USED IN ENHANCED OIL RECOVERY

Compound	Toxicity Data	Carcinogen/Response	Route of Exposure ^a	Major Use
Acrylamidediacetone		---		Surfactant additive
Acrylmethylpropyl sulfonic acid		---		Surfactant
Acrylonitrile	TLV 20 ppm	Neoplastigen	Inhalation	Surfactant additive/ contaminant
Aluminum citrate		---		Fraction micellar slug
Alkyltoluene sulfonate	LD50 2,480 mg/kg	---	Oral	Surfactant
Aniline	TLV 5ppm	Positive	Skin	Combustion, biocide
Ammonium hydroxide	rec'd std. 50ppm	---	Eye	Alkaline flooding
Acrolein	TLV 0.1 ppm	---	Inhalation	Bactericide
Alkyl dimethyl benzyl ammonium chloride	LDLo 50 mg/kg	---		Bactericide
Alkyl dichlorophenol (2,4)	TDLo 312 ug/kg	Positive	Skin	Bactericide; fraction micellar
Ammonium chromate		---		Cosurfactant
Alkyl phenoxypolyether	LD50 2,140 mg/kg	---	Oral, skin (rat)	Surfactant
Alkyl benzene sulfonates:				
p-n alkyl	LD50 1,850 mg/kg	---	Oral (rat)	Surfactant
linear alkyl	LD50 650 mg/kg	---	Oral (rat)	
Alkyl ortho xylene sulfonate	LDLo 500 ug/kg	---	Intraperitoneal (mouse)	Surfactant
Acrylamide copolymer	TLV 0.3 mg/m ³	---	Skin	Mobility control agent
Acrylamide homopolymer		---		Mobility control agent
Acrylic acid	DOT label: Corrosive	---		Surfactant additive
Alkyl aryl naphthenic sulfonate		---		Surfactant
Alpha olefin sulfonate		---		Surfactant
Alkylene oxide (see Ethylene oxide, Methylene oxide)		---		Surfactant
Benzene	TLV 25 ppm	Neoplastigen	Inhalation	Fraction micellar slug
n-Butanol	TLV 150 ppm	---	Inhalation	Cosurfactant
Benzyl alcohol	LDLo 500 mg/kg LC50 1,000 ppm/8h	---	Oral Inhalation (rat)	Cosurfactant
Cresol (hydroxytoluene)	TLV 5 ppm	Neoplastigen	Skin	Cosurfactant

TABLE 2 (Continued)

Compound	Toxicity Data	Carcinogen/Response	Route of Exposure ^a	Major Use
Cyclohexanol	TLV 50 ppm	---	Inhalation	Cosurfactant
	TCLo 75 ppm	---		
Calcium sulfate	TLV 10 mg/m ³	---	Inhalation	Bactericide
	TDLo 194 g/m ³ /10y	---		
Cadmium	TLV 0.05 mg/m ³	Positive	Inhalation	Bactericide
Carboxymethylcellulose	(Nontoxic) 2,700 mg/kg	---	Oral (rat)	Mobility control agent
Carboxypolyethylene (Carboxyvinyl polymer)	(Nontoxic) 2,700 mg/kg	---	Oral (rat)	Mobility control agent
Calcium chloride	TLV 10 mg/m ³	---	Oral, inhalation	Alkaline flooding
Cyclohexanone	TLV 50 ppm	---	Inhalation	Fraction micellar slug
Citric acid	LD50 11,700 mg/kg	---	Oral (rat)	Fraction micellar slug
Cyclohexane	TLV 300 ppm	---	Oral	Fraction micellar slug
p-Chloroaniline sulfate laurate		Positive		Surfactant
Cocodimethylbenzyl ammonium chloride		---		Bactericide
Decane		---		Fraction micellar slug
Dodecane		---		Fraction micellar slug
Alkyl dimethyl quaternary ammonium chlorides		---		Surfactant
Ditetradecyl dimethyl ammonium chloride		---		Surfactant
Dodecyl trimethyl ammonium chloride		---		Surfactant
Decyl benzyl sulfonic acid	LD50 2,000 mg/kg	---	Oral (mouse)	Surfactant
Diethyleneglycol sulfate	LD50 1,000 mg/kg	---	Oral (rat)	Surfactant
n-Dodecyl-diethyleneglycol sulfate	LD50 1,000 mg/kg	---	Oral (rat)	Surfactant
Dodecyl benzene sulfonate	TLm96 100-10 ppm	---		Surfactant
Diphenol picrylhydrazine		Positive		Combustion
Dimethyl hydrazine	TLV 0.5 ppm	Neoplastigen	Skin	Combustion
Diethylenetriamine	TLV 1 ppm	---	Skin	Combustion; bactericide
	LDLo 500 mg/kg	---		
Decanol (nonyl carbinol)	75 mg/3D-I	Neoplastigen	Skin	Cosurfactant
Diisobutylphenoxyethoxyethyl dimethyl benzyl ammonium chloride	LDLo 50 mg/kg	Neoplastigen	Oral, eye	Surfactant
Dextrane	(Nontoxic)	---		Mobility buffer
Deoxyribonucleic acid	(Nontoxic)	---		Mobility buffer

TABLE 2 (Continued)

Compound	Toxicity Data	Carcinogen/Response	Route of Exposure ^a	Major Use
Ethanol	TLV 1,000 ppm	Teratogen tests in progress	Inhalation	Cosurfactant
Ethylene oxide	LCLo 4,000 ppm	Possible	Inhalation	Demulsification
Ethanolamines	TLV 3 ppm; DOT: corrosive	---		Demulsification
Ethylenediamine	TCLo 200 ppm, TLV 10 ppm	---	Inhalation	CO ₂ removal
EDTA	2,000 mg/kg 7-14D	Teratogen	Oral (rat)	Preflushing agent
Glycerol	LD50 1,260 mg/kg	---	Oral	Mobility control agent; fraction micellar slug
Glyoxal (40%)	LD50 7,070 mg/kg	---	Oral, skin	Surfactant
Guar Gum	LD50 9,400 mg/kg	---	Oral (rat)	Mobility buffer
Glycerol disulfosuccinate monomyristate	(Low)	---		Surfactant
Glutaraldehyde	TLV 2 ppm	---	Skin	Bactericide;cosurfactant
Furfuryl alcohol	TLV 5 ppm	---	Skin	Cosurfactant
Fuel oil	12,500 mg/kg 5D	Mutagen	Oral, subcutaneous (mouse)	Cosurfactant
Formaldehyde	TLV 2 ppm	Neoplastigen	Inhalation	Bactericide;cosurfactant
Fluoride solutions	DOT: poison & oxidizers	---		Preflushing agent
1-hexanol	LDLo 500 mg/kg	---	Oral, skin	Cosurfactant
2-hexanol		---		Cosurfactant
Heptanol	LD50 3,250 mg/kg	---	Oral, rat	Cosurfactant
Hydroxyethylcellulose		Implant tumors	Subcutaneous	Mobility control agent
Hydrazine	TLV 1 ppm	Positive	Skin	O ₂ scavenger;combustion
Hydrogen peroxide	TLV 1 ppm; DOT: oxidizer	---	Inhalation	Alkaline flooding; combustion
Hexadecyltrimethyl ammonium chloride		---		Surfactant
Hexadecylnaphthalene sulfonate	LD50 2,320 mg/kg	---	Oral, rat	Surfactant
Hydroxyalkylsulfonate		---		Surfactant
Heptane		---		Fraction micellar slug
Isobutyl methacrylate	420 mg/kg	Teratogen	Ipr (rat)	Surfactant
Isoquinoline	350 mg/kg	---	Oral, skin	Alkaline flooding
Isobutanol	500 mg/kg	Positive	Oral, skin	Cosurfactant
Isopentanol	TLV 100 ppm	Positive	Inhalation	Cosurfactant
Isopropanol	TLV 400 ppm	---	Inhalation, skin	Cosurfactant
Lauryl polyethoxy sulfate	(Low)	---		Surfactant

TABLE 2 (Continued)

Compound	Toxicity Data	Carcinogen/Response	Route of Exposure ^a	Major Use
Lithium hydroxide		---		Steam flooding
Magnesium		---		Bactericide
Manganese		---		Bactericide
Monosaccharide		---		Mobility control agent
n-Methyltaurine oleamide		---		Surfactant
Monobutylphenyl phenol sodium sulfate		---		Surfactant
Morpholine stearate		---		Surfactant
Methyl methylacrylate	TLV 100 ppm	---	Inhalation-CNS	Surfactant
Methyl acrylate	75 ppm	---	Inhalation	Surfactant
p-Nonyl phenol	LD50 1,620 mg/kg	---	Oral (rat)	Cosurfactant
Nitrilotriacetic acid	LD50 1,470 mg/kg	Neoplastigen	Oral (mouse)	Fraction of micellar slug
Nitric acid	TLV 2 ppm; DOT: oxidizer and corrosive	---		Combustion
Nitrogen oxide	TLV 25 ppm; DOT: anesthetic gas	Teratogen	Inhalation (rat)	Combustion
Octadecyltoluene sulfonate		---		Surfactant
Octane		---		Fraction of micellar slug
Methyl nonyl ketone	LD50 5,000 mg/kg	---		
Methyl ethyl ketone	LD50 5,000 mg/kg	---		Fraction of micellar slug
Oxyethyl cellulose		---		Mobility buffer
1-octanol	LD50 790 mg/kg	---	Oral, skin	Cosurfactant
2-pentanol (amyl alcohol)	500 mg/24hour	---	Skin, eye, oral; moderate to severe effects (rodents)	Cosurfactant
Phenol	TLV 5 ppm	Positive	Skin	Cosurfactant, biocide
Pentadecyl phenol				Cosurfactant
Pentane	TLV 1,000 ppm	---	Inhalation-CNS	Fraction of micellar slug
Propane	TLV 1,000 ppm	---	Inhalation	Fraction of micellar slug
Potassium permanganate	TDLo 2,400 g/kg/D	---		Fraction of micellar slug
Potassium chromate	TLV 100 g	Possible	Oral, inhalation	Fraction of micellar slug
Polyoxyethylene	LD50 7,460 mg/kg		Oral (rat)	Fraction of micellar slug; cosurfactant; mobility control agent; demulsification

TABLE 2 (Continued)

Compound	Toxicity Data	Carcinogen/Response	Route of Exposure ^a	Major Use
Polyglycerol monolaurate	(Nontoxic)	---		Surfactant
Phenyl ethanol	LDLo 500 mg/kg LD50 1,790 mg/kg	---		Cosurfactant
Polyoxyethylene aryl phenol		---		Surfactant
Pentaerythritol monostearate	TLV 10 mg/kg	---		Surfactant
Polyethoxyalkylthiol		---		Surfactant
Polybutenesulfonate		---		Surfactant
Polyethylene glycol	LDLo 5,000 mg/kg	---	Oral	Mobility control agent
Polyacrylamide	(Low toxicity)	---		Mobility control agent
Polysaccharide	(Low toxicity)	---		Mobility control agent
Phenoxypolyethoxy ethanol	LD50 2,140 mg/kg	---	Oral (rat)	Mobility control agent
Paraformaldehyde	LDLo 50 mg/kg	---	Skin-severe	Bactericide
Pentachlorophenol	TLV 500 ug/m	Neoplastigen	Skin	Bactericide
Polyisobutylene in benzene	(High)	Possible		Mobility control agent
Quinoline	20 mg/24hour	Neoplastigen	Skin-mild Eye-severe Oral-carcinogen	Alkaline and thermal floods; biocide
Sodium lauryl sulfonate		---		Surfactant
Sodium sulfate oleylethanilide (tallow amine)	(Low)	---		Surfactant
Sodium glyceryl monolaurate sulfate		---		Surfactant
Sulfur trioxide	DOT: Corrosive	---		Surfactant additive
Styrene copolymer	LC50 120 mg/m ³ /10M	Neoplastigen	Inhalation (mouse)	Surfactant
Sodium hydrosulfite	LDLo 500 mg/kg	---	Inhalation	O ₂ scavenger; surfactant additive
Sodium hypochlorite	DOT: Corrosive	---		Bactericide
Sodium sulfate	LD50 5,939 mg/kg	---	Oral (rodent)	Fraction micellar slug
Sodium chloride	LDLo 500 12,357 mg/kg 23D	---	Oral--intraperi- toneal	Fraction micellar slug
Sodium nitrate	LDLo 500 mg/kg	---	Oral	Electrolyte
Sodium silicate (orthosilicate)	LD50 1,600 mg/kg	---	Oral (rodents)	Alkaline flooding
Sodium carbonate	LDLo 4,000 mg/kg	---	Oral (rat)	Alkaline flooding
Sodium borate	LDLo 500-709 mg/kg	---	Oral-mild toxic effects	Alkaline flooding

TABLE 2 (Concluded)

Compound	Toxicity Data	Carcinogen/Response	Route of Exposure ^a	Major Use
sec-Butanol	TLV 150 ppm	---	Inhalation	Cosurfactant
Sorbitan Fatty ester	TDLo 49g/kg/40M-I	---	Subcutaneous	Cosurfactant
Sodium bisulfite	LDLo 500 mg/kg	---	Oral	Alkaline flooding; O ₂ scavenger
Sodium hydroxide	TLV 2 mg/m ³ /15 min	---	Inhalation	Alkaline flood; preflushing agent; bactericide; electrolyte; thermal floods
Sodium dichlorophenol				Bactericide
Sodium pentachlorophenol	LD50 210 mg/kg	---	Oral (rat)	Bactericide
Triethyl borane	LD50 235 mg/kg LC50 2,800 mg/m ³	---	Oral	Bactericide
		---	Inhalation	Combustion
Triethyl aluminum		---		Combustion
Toluene sulfonic acid		---		Surfactant
Tridecylbenzyl sulfonate		---		Surfactant
Triethanolamine laurate	5,000 mg/kg	---	Oral	Surfactant
Triethanolamine myristate		---		Surfactant
Triethanolamine oleate	5,000 mg/kg	---	Oral	Surfactant
p-Toluidine sulfate laurate		---		Surfactant
Toluene	TLV 100 ppm	CNS	Skin	Fraction of micellar slug
Tallow amines	LD50 1,850 mg/kg	---	Oral (rat)	Surfactant
Xylidine	TLV 5 ppm LD50 50 mg/kg	---	Skin	Combustion
Xylene	100 ppm/10 min	---	Inhalation	Surfactant
Xylene sulfonate				Surfactant
Xanthan gum	(Low)	---		Mobility control agent

Notes: TLV = Threshold limit value.
 LD50 = The dose at which 50 percent of the subject animals die.
 LDLo = The dose at which less than 50 percent of the subject animals die.
 TCLo = Low threshold concentration.
 TDLo = Low threshold dose.
 --- = No evidence of carcinogenic activity found.
 CNS = Central nervous system.

^aUnless otherwise noted, in "Route of Exposure" column, data is human health data.

Source: Silvestro 1980.

Biocides pose significant risks. Phenol toxicity is discussed in the Refinery Operations section of this report under Health Effects. Chlorinated phenols such as pentachlorophenol and 2,4,5-trichlorophenol (2,4,5-T) may be contaminated with chlorinated dioxins and dibenzofurans (also discussed in the Refinery Operations section). Glutaraldehyde, formaldehyde, and paraformaldehyde may act as sensitizers and carcinogens.

Polysaccharide-based and polyacrylamide agents pose significant inhalation hazards. Xanthan gums have been reported to cause disease similar to polymer and metal fume fevers. Hydrazine and quinoline employed in in situ combustion are carcinogenic in animal experiments and potential sensitizers. In significant quantities, chelating agents such as ethylenediaminetetracetic acid (EDTA) may sequester mineral cotactors in mucosal barriers, leading to the enhanced absorption of other toxic agents.

Chemical reactions and synergistic toxic effects among the various compounds employed in oil extraction are largely unknown, as are those of their contaminants, crude oil and its contaminants, and compounds encountered in drill cuttings. Drilling rig and other oil extraction workers' exposures to toxic agents and resulting adverse effects have received little study and remain largely uncharacterized.

A number of factors may be contributing to unassessed occupational health problems among oil rig and field workers. Domestic oil and gas drilling and extraction have recently experienced an upsurge in activity and this trend is expected to continue. Experienced and skilled field workers are in high demand worldwide, and it may be presumed that many oil rig and field workers lack extensive knowledge and experience with the mechanical, flammable, explosive, and toxic hazards they routinely encounter. Much drilling, especially exploratory drilling, is performed by small, independent operators. These factors, combined with the proprietary nature of drilling muds and enhanced oil recovery compounds, may contribute to unassessed occupational health problems among oil rig and field workers. These problems may be difficult to assess, as these workers are highly mobile and often live and work in isolated, undeveloped areas, lacking sophisticated medical facilities and expertise.

The use of miscible fluids to aid crude petroleum extraction entails occupational exposures distinct from those associated with waterflooding. Two such technologies are hydrocarbon and CO₂ flooding, which use miscible gases as the driving fluids. There is a risk from fire and explosion associated with miscible hydrocarbon injection. The more widely used CO₂ flooding entails risks of worker asphyxiation. This may occur either through handling, on-site

storage, or during the actual injection process (U.S. Department of Energy 1978). In addition to the direct use of CO₂, hydrogen sulfide may become mixed with the injected gas in the reservoir formation. These mixed gases may then be recycled back into the reservoir. Should this occur, workers may be exposed to the toxic effects of H₂S, as discussed in the Refinery Operations section of this report under Health Effects.

Water miscible (micellar/polymer) and thermal (steam and in situ) oil extraction methods pose significant health hazards both for the worker and the public. The micellar/polymer technology utilizes many different groups of chemicals, e.g., surfactants, cosurfactants, mobility buffers, electrolytes, pre-flushing compounds, bactericides, and various hydrocarbons that may be part of the micellar slug (Schumacher 1978). Within each of these groups there are many specific compounds that can be used (U.S. Department of Energy 1978). In general, it has been estimated that two pounds of chemicals are injected into a reservoir for each barrel of recovered oil (U.S. Department of Energy 1978).

Oil extraction may result in significant fugitive emissions of crude oil hydrocarbons and volatile crude oil constituents, including potentially carcinogenic benzene. In addition, neurotoxic lower alkanes may evaporate from a number of sources. PAHs and other heavier compounds may be suspended in aerosols, condensed on particulates, or volatilized due to high temperatures. Volatile and liquid nitrosamines may form in extracted crude oil and during treatment.

Public Health Hazards

Depending on how widespread the uses, amounts, and types of chemicals utilized and the pollutants produced, oil production technologies may have adverse impacts on public health. The thermal technologies, especially steam injection, may result in hazardous exposures.

Currently, steam injection is the most widely used method for enhanced oil recovery in the U.S. and is primarily centered in California (U.S. Department of Energy 1978). Approximately 15 gallons of crude oil, containing up to 2 percent sulfur, must be burned in steam boilers to inject enough steam to produce 1 barrel (42 gallons) of oil (U.S. Department of Energy 1978). Such combustion produces large amounts of airborne emissions. Among the pollutants produced are oxides of sulfur and nitrogen and particulate matter (U.S. Department of Energy 1978). Another study on emissions from such combustion showed that aldehydes, polycyclic aromatic hydrocarbons such as benzo(a)pyrene, carbon monoxide, hydrocarbons, and

sulfur trioxide were produced (Schumacher 1978). In addition to any direct exposure effects from these compounds, indirect effects may occur as a result of atmospheric interactions or transformations. The indirect effects associated with airborne transport of organics and combustion products are not well understood, but it is known that specific airborne organics, such as the polycyclic aromatic hydrocarbons, have induced a variety of cancers (Stokinger and Coffin 1968; Laskin et al. 1970). Atmospheric oxidants have also been shown to initiate, or act as co-carcinogens for, the carcinogenic action of these hydrocarbons (Ayers and Buehler 1970; Altshuller and Bufalini 1971).

Other health impacts also have been studied. Hammer, et al. (1974) found coughing and chest discomfort to exist when healthy individuals were exposed to combustion-related oxidant concentrations between 0.25 and 0.39 ppm. In addition, the level of aldehydes has been linked with the degree of eye irritation (Renzetti and Bryan 1961).

Although in situ combustion, another thermal recovery method, occurs deep within the oil reservoir, it also may produce emissions at the production well. In gaseous waste streams analyzed from 31 in situ combustion projects, carbon monoxide, carbon dioxide, oxygen, and light hydrocarbons (methane, ethane, and propane) were detected.

A large potential for adverse impacts from enhanced recovery (excluding air pollution from the steam injection and in situ combustion processes) may reside in chemically-contaminated water that may infiltrate potable water supplies. The leaching and transport potential of various petroleum extraction chemicals or emission products into underground freshwater supplies are considered in the next section. The toxicity of crude oil constituents, drilling mud compounds, and oil recovery agents may be significantly increased when water is chlorinated prior to public use. Carcinogenic halogenated methanes, chlorinated phenolics, and other compounds may be formed. The contamination of any freshwater source, especially if it is used as a source of drinking water, could have potentially serious public health consequences. Health effects would depend on such factors as the amount and specific toxicity of the compounds in question. Fugitive emissions of hydrocarbons and other agents from used brine and fluids, crude oil, and leaking equipment may affect the health of those living near oil wells. The health and environmental effects of fugitive emissions are discussed in the Refinery Operations section of this report.

Health Effects of Natural Gas Production

The basic exploratory and drilling procedures utilized for natural gas do not differ substantially from those for oil (University of Oklahoma 1975). Thus, many potential health effects due to natural gas extraction have been discussed.

Potential health effects may result from separating dissolved natural gas from crude oil at the production site. How the separated gas is further treated at the production site determines how potentially hazardous the operations may be to workers and the nearby public.

Of direct concern from the standpoint of health impacts is the fact that natural gas may have varying concentrations of hydrogen sulfide associated with it. One study covering different geographical areas reported representative percent-by-volume data ranging from 0 to 35 percent (Leggett and Williams 1979). If the gas is processed rather than flared, the toxic hydrogen sulfide component will be isolated and concentrated. Aside from any accidental release of gas, a major health concern is related to how the gas is flared and its combustion products. The amounts of sulfur oxides and hydrogen sulfide emitted by flaring have been estimated. Assuming that natural gas contains an average of 0.5 mole percent of sulfur, approximately 250 million cubic feet per year of gaseous sulfur oxides and hydrogen sulfide are vented to the atmosphere from flares and fugitive losses (Wilkins 1977).

Potential health impacts from enhanced recovery methods, fracturing, and directional drilling must be considered in addition to those from conventional recovery techniques. These are new technologies for gas recovery involving undefined health hazards related to the use of cryogenic and exotic fluids, and hazards associated with high pressures. At this point it would seem that many of the hazards associated with more conventional methods (e.g., hydrogen sulfide toxicity, hydrogen sulfide combustion, and oil combustion-related emissions) also apply to the new technologies.

Summary of Research Needs

Health Effects Data

Some health effects data for the petroleum industry are reported for the operations subject to recordkeeping requirements of the Occupational Safety and Health Administration (OSHA). The data include the number of employees, hours worked, recordable injuries and illnesses, incident rates for fatalities, and information on lost workdays and restricted activity. These data are reported by Standard Industrial Classifications (SIC; U.S. Office of Management and Budget

1972). With respect to drilling (SIC 1381) and exploration and production operations (SIC 1311), data from both onshore and offshore drilling rigs are commingled and there is no separation of accident data from ancillary operations such as brine injection systems and brine transport and disposal.

Both onshore and offshore activities have diverged markedly over the last decade with respect to the nature and extent of risks. This is especially true as offshore exploration and production move into the deeper waters of the outer continental shelf.

An information gathering and reporting infrastructure is needed for collecting and processing health effects data. More explicit data also are needed with respect to the nature and extent of illnesses and diseases. This information would be useful in retrospective epidemiological studies.

Effects of Drilling Muds and Enhanced Oil Recovery Agents

A study is needed concerning occupational exposure to drilling muds and enhanced oil recovery agents. Documentation is needed on the frequency and duration of worker exposures. The study should include a retrospective epidemiological survey to assess potential health risks associated with operational handling and accidental exposures.

Exposure to Toxic Chemicals

Crude oil extraction and enhanced recovery methods involve worker exposure to many kinds of potentially toxic substances, including sequestering agents, anticorrosives, phenols, cosurfactants, bactericides, and various polycyclic hydrocarbons associated with crude petroleum. Although many basic research studies deal with the toxic effects of some of these materials, research has not focused on process-specific worker exposures to these substances. An in-depth assessment involving field study and measurements is needed, which focuses on identification of the toxic and carcinogenic chemicals utilized in secondary and tertiary recovery techniques and on an assessment of health risks associated with occupational exposure to these materials.

Public Health Considerations

Over the last decade, numerous health assessment studies have been performed which relate to potential risks to public health as a result of oil production. These generally have focused on production near urban areas in Texas and southern California. Most of these have been conducted on the state level and have focused on conventional oil and gas production.

With the increasing use of sophisticated advanced recovery techniques, many new kinds and new combinations of gases and aerosols may be released to the atmosphere. The effects of these on adjacent communities and their interaction with urban pollutants should be addressed.

Interactions of Toxic Agents

Chemical interactions and synergistic reactions among the numerous substances encountered in crude oil need study. Heat, pressure, and the complex chemical mixing that occurs during drilling may lead to the formation of unrecognized toxic substances.

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ECOLOGICAL EFFECTS OF ONSHORE DEVELOPMENT

Aquatic Biota

This section focuses on the effects of petroleum on freshwater biota, as well as the effects of compounds associated with petroleum production.* Among the factors to be addressed are:

- o The source, composition, and relative toxicities of organic and inorganic petroleum components in the freshwater environment;
- o The manner and degree by which such components may be taken up and transformed by organisms; and
- o The various effects (or lack of effects) that petroleum or associated compounds may have on various organisms.

In petroleum production the pollutant of greatest potential concern, not only because of its volume, but also its toxicity, is the crude oil itself. Crude petroleum is a complex mixture of organic, inorganic, and metallic compounds, with the organics predominating. Some of its major organic groups are: the aliphatic hydrocarbons, cyclic paraffin hydrocarbons, aromatic hydrocarbons, naphthene-aromatic hydrocarbons, resins, asphaltenes, and heteroatomic compounds (Bestougeff 1967). "Average" crude oil may also be characterized by the molecular size of its organic components. Gasolines (C_5 to C_{10}) comprise 30 percent; kerosenes (C_{10} to C_{12}), 10 percent; light distillate oils (C_{12} to C_{20}), 15 percent; heavy distillate oils (C_{20} to C_{40}), 25 percent; and residuum oil, 20 percent (Valkovic, 1978). These relative proportions are helpful as an indicator of a particular crude oil's toxicity to various types of freshwater organisms. For example, in the event of a spill, some of the lighter components of oil may evaporate rapidly, presenting a different length of exposure (but not necessarily of toxicity) than heavier components.

Petroleum Constituents

Of all the organic fractions comprising petroleum, the aromatic hydrocarbons appear to be the most acutely toxic compounds (U.S. Environmental Protection Agency 1972). Such aromatics may exist in relative abundance; for example, benzene constitutes 20 percent or more of the total aromatics found in crude oil (Brockson and Bailey 1973).

*Effects on water quality are discussed below under Transport and Transformation.

In addition to the organics, crude petroleum also has a large number of trace elements associated with it. The elements found in petroleum vary in number, concentration, and potential toxicity (Valkovic 1978). However, two metals--vanadium and nickel--exist in such high concentrations that their ratio to each other is often used to characterize crude petroleum (Valkovic 1978). Both of these metals can have toxic effects on freshwater biota which are discussed below.

The concentration of metals in crude oil may vary with both the geographic source and geological age of the petroleum. Vanadium is the element in greatest abundance, with levels as high as 1,100 ppm reported (Filby and Shah 1975). Nickel is less abundant than vanadium, but its content is still high compared to other metals. Some crude oil has been reported to contain 350 ppm (Valkovic 1978). These metals are not uniformly distributed among the various classes of organic compounds with which they are associated, but usually reside in the higher-weight molecular compounds such as resins and asphaltenes (Filby and Shah 1975).

Consideration of all crude oil components reveals a great variation in the fuel's potential effects on aquatic organisms. It has been suggested that the severity of petroleum's effects may increase in sequence, from mammals, which are highly tolerant; through finfish, plankton, and benthos; to birds, which are highly affected (American Institute of Mining Engineers 1975). A statement of this type is at best a generalization, and it should again be emphasized that different crude oils consist of varying amounts of light and heavy components of different molecular size. Consequently, the effects of crude oil components will differ in their toxicity to specific groups of organisms depending on many factors (e.g., amount of coating; rates of uptake, accumulation, elimination). For example, the low boiling, water soluble components of a crude oil may be more acutely toxic due to their rapid uptake. This is especially true when refined oils, which contain a greater percentage of these low boiling compounds, are spilled (Brown, V.M., 1976). Although components of crude oil may be lethal to aquatic mammals and birds over a long period of time, many of these organisms die soon after an oil spill as a result of suffocation, exposure to cold, and drowning.

In the production of crude oil, there are occasions when chemicals used in its production become mixed with it. In any discussion, therefore, of the ecological effects of crude petroleum, one must consider the potential effects of these "foreign" components. The problem of evaluating the toxicity of petroleum and any of these associated compounds is further complicated by the question of synergistic reactions, i.e., the combination of various components--whatever their source--may have greater, lesser, or differing effects than any of the components alone.

Naturally occurring freshwater compounds could combine with various petroleum associated compounds to either mitigate or intensify potentially toxic reactions. Freshwater systems such as those affected by onshore oil and gas activities are excellent examples of both of these phenomena. There are wide variations in the levels of calcium and magnesium salts in freshwater, but whatever their concentration, they may affect the toxicity of foreign elements such as crude oil organics and metals that may enter such systems. If such petroleum-derived materials enter freshwater in a spill, the natural hardness of the receiving water may be one determinant of potential toxicity. It appears that an inverse relationship exists between the toxicity of trace metal cations and water hardness. That is, the greater the hardness of the water, the less toxic are the cations of various trace metals to freshwater life.

In reality, the hardness of freshwater is often ascertained by measuring the calcium content of the water. It has been shown that in soft acid water (low calcium content) there is an observed toxicity to fish even when trace metals are at relatively low concentrations (Brown, V.M., 1976). It has also been reported that the rates and levels of uptake of various heavy metal radionuclides appear to be inversely related to the calcium concentration of the water (Brown, V.M., 1976). Concomitantly, any of a number of naturally occurring compounds within crude oil may combine with chemicals used to either produce them, or clean them up in the event of a spill. Such chemical combinations may present different freshwater systems with differing degrees of toxic stress. Table 3 presents a synopsis of assorted effects on different groups of organisms caused by crude petroleum, some of its major constituents, and various associated compounds used in its production.

In an oil spill, not all plants and animals are affected equally; some are impacted in different ways and by different mechanisms. For example, waterfowl may be killed quickly during the initial stages of an aquatic oil spill due to the loss of natural protective oils from their feathers (American Petroleum Institute 1976). Birds thus contaminated usually die from exposure, rather than from the uptake and accumulation of toxics in the oil.

Some constituents of crude oil also may affect waterfowl by inhibiting successful adult reproduction. Preliminary experiments on mallard eggs, to which microliter amounts of crude oil were applied, have shown dose-related mortality (Alber and Szaro 1976). It is believed that such mortality results from toxic components within the crude oil, not embryo suffocation from oil covering the eggs. When the eggs were treated with a mixture of paraffins like those found in crude oil, only a small decrease in reproduction resulted (Alber and Szaro 1976). It has therefore been suggested that the embryotoxic

TABLE 3

EFFECTS ON SELECTED FRESHWATER BIOTA FROM PETROLEUM AND ASSOCIATED CONSTITUENTS

Freshwater Organisms	Compound(s) Examined	Reported Toxicity Values or Ranges	Sublethal Effects/ Potential Effects	Reference
Algae				
<u>Clamydomonas angulosa</u> <u>Chlorella vulgaris</u>	Various straight and branched chain alkanes, cyclo-alkanes, aromatics and polynuclear aromatics:	Toxicity measured as the concen- tration (x) necessary to cause 50% photosynthetic reduction:	It was found that hydro- carbons with a low solubility (on a molar basis) were more toxic than the high solubility compounds. It was further noticed that the solubilities of the com- pounds tested extended over eight orders of magnitude.	Hutchinson et al. 1980
<u>C. angulosa</u>	Dodecane	(mmol/m ³) 0.033		
	Tetradecane	0.056		
	Naphthalene	75		
	Phenanthrene	5.3		
	Anthracene	1.34		
	Pyrene	1		
<u>C. vulgaris</u>	Dodecane	0.039		
	Tetradecane	0.131		
	Naphthalene	150		
	Phenanthrene	5.8		
	Anthracene	3		
	Pyrene	1.64		
<u>Nitzschia linearis</u>	Anionic ABS (surfactant)	-	1.9 mg/l reduced growth by 21%; 14 mg/l by 100%	Nelson-Smith 1973
<u>Clamydomonas</u> sp. <u>Scenedesmus</u> sp. <u>Chlorella</u> sp.	Non-ionic surfactants	All three organisms killed at 200 ppm.	Growth suppressed at concentrations as low as 5 ppm.	Nelson-Smith 1973

TABLE 3 (Continued)

Freshwater Organisms	Compound(s) Examined	Reported Toxicity Values or Ranges	Sublethal Effects/ Potential Effects	Reference
Crustacea				
Daphnids <u>Daphnia magna</u>	Linear alkylbenzene Sulfonate (surfactant)	- -	Uptake of compound occurred and was found to be a function of chain length and exposure concentration	Comotto et al. 1979
Mollusca				
Fresh Water Mollusca <u>Cipangopalundina</u> <u>chinensis</u>	The concentration of polynuclear aromatic hydrocarbons (PAHs) in sediment and molluscs.	-	Bioaccumulated concentra- tions of some PAHs were from 15 to 200 times higher in the molluscs than in the sediment.	Kalas et al. 1980
Fish				
Pink Salmon Fry <u>Oncorhynchus gorbuscha</u>	Prudhoe Bay crude oil	Median tolerance limit (TLM) ranged from 48-110 ppm.	Avoidance effects on large fry at 1.6 ppm; possibility exists that avoidance may disrupt migration patterns.	Rice 1973
Freshwater fish	Crude oil	Concentrations as low as 0.3 mg/l found toxic.	-	U.S. Department of the Interior 1972
Chinook Salmon. <u>Oncorhynchus tshawytscha</u>	Benzene	-	Found 86% increase in res- piration rate over controls after exposure time of 48 hrs to 5 ppm benzene. Exposure to 10 ppm benzene for periods greater than 48 hrs caused narcosis resulting in respira- tory decrease.	Brockson and Bailey 1973

TABLE 3 (Continued)

Freshwater Organisms	Compound(s) Examined	Reported Toxicity Values or Ranges	Sublethal Effects/ Potential Effects	Reference
Bluegills <u>Lepomis macrochirus</u>	Benzene Cyclohexane Phenol Toluene	22.49 14.72 23.88 24.00	-	Pickering and Henderson 1966
Goldfish <u>Carassius auratus</u>	Benzene Cyclohexane Phenol Toluene	14.42 22.33 44.49 57.68	-	Pickering and Henderson 1966
Guppies <u>Lebistes reticulatus</u>	Benzene Cyclohexane Phenol Toluene	16.60 57.68 39.19 59.30	-	Pickering and Henderson 1966
Pink salmon fry <u>Oncorhynchus gorbuscha</u>	Water soluble fractions (WSF) from Cook Inlet crude oil	96-hour median tolerance limit (TLm) 2.92 ppm	-	Rice 1976
Brown trout <u>Salmo trutta</u>	Tia Juana medium Venezuela crude oil used in laboratory investigations		Both field investigations (from an oil polluted lake) and laboratory tests confirmed a significant increase in aryl hydrocarbon hydroxylases (AHH) in fish subjected to petroleum versus controls.	Payne and Penrose 1975
Rainbow trout <u>Salmo gairdneri</u>	Benzo(a)pyrene	-	Induction of aryl hydrocarbon hydroxylase by benzo(a)pyrene and metabolism (hydroxylation) of this compound in liver.	Malins 1977

TABLE 3 (Continued)

Freshwater Organisms	Compound(s) Examined	Reported Toxicity Values or Ranges	Sublethal Effects/ Potential Effects	Reference
Rainbow trout <u>Salmo gairdneri</u>	2-Methylnaphthalene, Naphthalene	-	Half-lives of pollutants in fish exposed to pollu- tants for 9 hours were less than 24 hours; but exposure to compounds for 4 weeks produced half-lives (elimi- nation) of hundreds of hours. "Parent" compounds were often found as metabolites within tissue.	Melancon and Lech 1979
Carp <u>Cyprinus carpio</u>				
Bluegills <u>Lepomis macrochirus</u>	Various surfactants Linear alkyl benzene sulfonate, alkyl ethoxylate sulfate, amine oxide, trisodium nitrilotri-acetate		Some surfactants tested can induce increases in ventila- tion (respiratory) rates.	Maki 1979
Trout	Anionic surfactants	-	Immobilization of sperm and reduced fertilization rate.	Nelson-Smith 1973
Fathead Minnows <u>Pimephales promelas</u>		96-hr median tolerance limit (TLM) mg/l:		Pickering and Henderson 1966
	Benzene	33.47		
	Cyclohexane	32.71		
	Phenol	34.27		
	Toluene	34.27		

TABLE 3 (Concluded)

Freshwater Organisms	Compound(s) Examined	Reported Toxicity Values or Ranges	Sublethal Effects/ Potential Effects	Reference
Birds				
Mallard ducks <u>Anas platyrhynchos</u>	Vanadium	-	Significantly alters lipid metabolism.	White and Dieter unpublished (as cited in Dieter 1976)
Mallard ducks <u>Anas platyrhynchos</u>	Crude oil		Toxic organics in crude oil may have embryotoxic effects at very low concentrations on mallard eggs.	Dieter 1976

components in crude oil may reside in the aromatic rather than the paraffin portion of the petroleum. Studies on herring gulls from Lake Ontario may also implicate specific petroleum constituents as potential factors in the low reproductive rate noted there among the gulls. Investigations to determine the reasons for such low reproductive success led to an analysis of the gulls' body fat (lipids). Among 14 polynuclear aromatic compounds identified were 6 major aromatic compounds associated with petroleum: naphthalene, 2-methylnaphthalene, anthracene, benzo(a)fluorene, benzo(a)pyrene, and 9,10-diphenylanthracene (Fox et al. 1975).

Effects of Petroleum Extraction Chemicals

As discussed previously, chemical agents employed in drilling muds and enhanced oil extraction may be toxic to animals and humans. Toxicity values for many of these agents as they affect fish and daphnia are shown in Table 4. The aquatic toxicity of several hydrocarbons and other compounds is significantly increased when water is chlorinated for disinfection.

Effects of Metals

In addition to the diverse organic compounds in petroleum, there is a large and variable number of trace elements. For example, vanadium, varying in proportion from one crude oil to another, is usually in the highest concentration relative to other trace metals. It has been shown that this element can significantly alter lipid (cholesterol and triglyceride) metabolism in specific waterfowl such as mallard ducks (White and Dieter, as cited in Dieter 1976). In these experiments, cholesterol values were measured for non-laying and laying mallard hens. The former averaged 119 mg per dry liter and the latter, 38 mg per dry liter. These values were determined to be normal, average values for these two conditions. In the ensuing experiments, the laying hens were fed 100 ppm of vanadyl sulfate. Average concentrations of cholesterol were then measured at intervals of 3, 6, 9, and 12 weeks. It was found that there was no longer much of a difference between the laying hens and their non-laying counterparts, with cholesterol averaging 91 mg per dry liter. In a similar pilot study the same alteration of lipid metabolism occurred when mallard hens were fed 10,000 ppm of crude oil. In addition, they laid fewer eggs than normal (Dieter 1976).

It is apparent that any such oil-induced changes could have profound effects on the reproductive capacity of freshwater waterfowl, especially when vanadium may occur in relatively high proportions. Since many waterfowl both live and reproduce in or around freshwater rivers, lakes, and marshes, the potential for direct kills or

TABLE 4

TOXIC EFFECTS OF PETROLEUM EXTRACTION CHEMICALS TO FISH AND DAPHNIA

Organic Compound	Type of Organism Used in Test ^a	Median Tolerance Limit (TLM) ^b (milligrams per liter)	Length of Test (hours)	No Mortality (milligrams per liter)	100 Percent Mortality (milligrams per liter)	Remarks ^c
Acids and salts						
Acetic acid	Creek chub	...	24	100	200	Detroit River
Acetic acid	Mosquito fish	251	24	...	...	Turbid Oklahoma
Acetic acid	Goldfish			10	...	Hard water
Benzoic acid	Mosquito fish	240	24	...	...	Turbid Oklahoma
Propionic acid	Daphnia magna	130	24	...	...	...
Alcohols						
n-Amyl alcohol	Creek chub	...	24	350	500	Detroit River
n-Butyl alcohol	Creek chub	...	24	1,000	1,400	Detroit River
tert-Amyl alcohol	Creek chub	...	24	1,300	2,000	Detroit River
tert-Butyl alcohol	Creek chub	...	24	3,000	6,000	Detroit River
Ethyl alcohol	Creek chub	...	24	7,000	9,000	Detroit River
Diethylene glycol	Mosquito fish	>32,000	24	...	...	Turbid Oklahoma
Isopropyl alcohol	Creek chub	...	24	900	1,100	Detroit River
Methyl alcohol	Creek chub	...	24	8,000	17,000	Detroit River
n-Propyl alcohol	Creek chub	...	24	200	500	Detroit River
Aldehydes and ketones						
Acetaldehyde	Pinperch	7C	24	...	...	Seawater
Acetone	Mosquito fish	13,50C	24	...	...	Turbid Oklahoma
Furfural	Mosquito fish	44	24	...	...	Turbid Oklahoma
Furfural	Bluegill sunfish	32	24	...	...	Tap water
Methylethyl ketone	Bluegill sunfish	5,64C	24	...	...	Tap water
Amines and amides						
Diethanolamine	Mosquito fish	1,80C	24	...	...	Turbid Oklahoma
Diethanolamine	Bluegill sunfish	2,10C	24	...	...	Tap water
Hydrocarbons						
Benzene	Bluegill sunfish	20	24	...	...	Tap water
Cyclohexane	Mosquito fish	15,500	24	...	...	Turbid Oklahoma
Heptane	Mosquito fish	4,924	24	...	...	Turbid Oklahoma
Kerosene	Bluegill sunfish	2,990	24	...	...	Tap water
Naphthalene	Mosquito fish	220	24	...	...	Turbid Oklahoma

TABLE 4 (Continued)

Organic Compound	Type of Organism Used in Test ^a	Median Tolerance Limit (TLM) ^b (milligrams per liter)	Length of Test (hours)	No Mortality (milligrams per liter)	100 Percent Mortality (milligrams per liter)	Remarks ^c
Nitriles						
Acrylonitrile	Pinperch	24.5	24	...	...	Seawater
1-Cyano - 1,3-butadiene	Pinperch	71.5	24	...	...	Seawater
Miscellaneous						
Pyridine	Mosquito fish	1,350	24	...	...	Turbid Oklahoma
Sodium hydroxide	Bluegill sunfish	43 (OH)	24	...	...	Tap water
Sodium hydroxide	Creek chub	...	24	20	40	Detroit River
Phenolic compounds						
Cresol	Mosquito fish	24	24	...	...	Turbid Oklahoma
Phenol	Bluegill sunfish	19	24	...	...	Tap water
Phenol	Creek chub	...	24	10	20	Detroit River
Pentachlorophenate	Fathead minnow	0.33	24	...	...	Detroit River
Phenol	Bluegill sunfish	22.7	24	...	...	Std. ref. water
o-Chlorophenol	Bluegill sunfish	8.2	24	...	...	Std. ref. water
o-Nitrophenol	Bluegill sunfish	66.9	24	...	...	Std. ref. water
Various other phenolics	...	...	...	...	...	...
Silver nitrate	Daphnia magna	0.0051	64	...	...	Lake Erie water
Sodium chloride	Daphnia magna	3,412	24	...	...	Lake water
Sodium dodecyl benzene sulfonates	Creek chub	4	24	...	...	Detroit River
Sodium hydrosulfide	Mosquito fish	...	24	4	10	Detroit River
Sodium chromate	Mosquito fish	7,700	24	...	...	Turbid Oklahoma
Sodium fluoride	Mosquito fish	750	24	...	...	Turbid Oklahoma
Sodium hydrosulfide	Mosquito fish	1,240	24	...	...	Turbid Oklahoma
Sodium oleate	Mosquito fish	206	24	...	...	Turbid Oklahoma
Sodium pentachlorophenate	Shiners	...	120	5	...	Hard water
Sodium thiosulfate	Bluegill sunfish	...	24	0.2	0.4	Tap water
Sodium phosphate	Shiners	...	120	5	...	Hard water
Sodium triphosphate	Mosquito fish	720	24	...	...	Turbid Oklahoma
Toulene	Mosquito fish	720	24	...	...	Turbid Oklahoma
	Mosquito fish	1,340	24	...	...	Turbid Oklahoma
Sodium sulfonates						
Sodium n-butyl sulfonate	Daphnia magna	...	100	7,827	1,637	Std. ref. water
Sodium benzene sulfonate	Daphnia magna	...	100	8,000	1,895	Std. ref. water

TABLE 4 (Continued)

Organic Compound	Type of Organism Used in Test ^a	Median Tolerance Limit (TLm) ^b (milligrams per liter)	Length of Test (hours)	No Mortality (milligrams per liter)	100 Percent Mortality (milligrams per liter)	Remarks ^c
Sodium p-chlorobenzene sulfonate	Daphnia magna	...	100	3,007	1,687	Std. ref. water
Sodium m-nitrobenzene sulfonate	Daphnia magna	...	100	5,618	1,000	Std. ref. water
Sodium phenol sulfonate	Daphnia magna	...	100	5,623	556	Std. ref. water
Sodium naphthalene-sulfonate	Daphnia magna	...	100	308	55	Std. ref. water
Sodium anthraquinone-a-sulfonate	Daphnia magna	...	100	30	10	Std. ref. water
Sulfuric acid	Bluegill sunfish	49(SO ₃)	24	...	...	Tap water
Sulfuric acid	Goldfish	...		133	...	Hard water
Additional compounds						
Alkyl benzene sulfonate	...	3.5	24	...	...	Hard water
Aluminum sulfate	Bluegill sunfish	...	168	100	250	Tap water
Ammonium acetate	Mosquito fish	238	24	...	...	Turbid Oklahoma
Ammonium sulfide	Mosquito fish	248	24	...	...	Turbid Oklahoma
Ammonium thiocyanate	Mosquito fish	910	24	...	...	Turbid Oklahoma
Formaldehyde	Rainbow trout	...	72	10	50	Hard water
Methyl mercaptan	Minnows	...	120	0.5	...	Hard water
Nitriles						
Acetonitrile	Bluegill sunfish	1,850	24	...	...	Soft water
Acrylonitrile	Bluegill sunfish	25	24	...	...	Soft water
Benzonitrile	Bluegill sunfish	78	24	...	...	Soft water
Oxydipropionitrile	Bluegill sunfish	4,300	24	...	...	Soft water

^aCreek chub (*Semolilus atromaculatus*), mosquito fish (*Gambusia affinis*), goldfish (*Carassius auratus*), bluegill sunfish (*Lepomis macrochirus*), rainbow trout (*Salmo gairdnerii*).

^bMedian tolerance limit (TLm) is the concentration that will kill half the fish in the time shown.

^cFor complete data, see test conditions described in the references cited on page 20-15 of Silvestro 1980.

Source: Silvestro 1980.

decreased reproduction from oil spills could be large. This could especially be true along the major flyways which are the prime routes used by waterfowl during spring and autumnal migrations.

Mobility of Organisms

Organisms which spend their entire life cycle within aquatic systems (e.g., fish, plankton) and the benthic community may be impacted in different ways and to different degrees than other less habitat-restricted organisms such as waterfowl. Often the effect of spilled petroleum on wholly aquatic organisms is a function of their mobility. For example, fish may be able to avoid the area of a spill before contamination occurs, but plankton and many members of the benthos (e.g., freshwater clams, gastropods, and other molluscs) are sessile or move very slowly. Groups such as these will be severely impacted if subjected to toxic petroleum compounds.

Even fish, which have a relatively high degree of mobility, may be severely impacted by an aquatic spill. One reason for this lies in the great divergence in physical characteristics of freshwater, as opposed to marine systems. Freshwater ecosystems vary in area, water depth, temperature, pressure, ion concentrations, and other parameters, especially when compared to marine systems. Such physical and chemical variations may enhance the pollution stress placed on even mobile organisms in a spill situation. Fish may experience interference with respiration when epithelial gill surfaces are covered with petroleum; aquatic oxygen depletion may occur from petroleum's organic constituents, and there can be more direct and rapid toxic effects due to the soluble compounds within oil (U.S. Department of the Interior 1972). In the general area of toxicity, the importance that various physical factors may have in augmenting toxic effects may not be adequately appreciated. Simple physical phenomena, such as winds, or the turbulence of flowing streams or rivers, may greatly increase the mixing or dispersion of oil throughout the water column.

Effects of Surfactants

In severe spills, chemical dispersants or surfactants have been deliberately employed to disperse or solubilize the oil. Yet, the toxicity of oil and its degradation products are directly related to the amount of its dispersion throughout the water column. It is reported that, the greater the emulsification and dispersion of oil alone, the greater the toxicity (Tarzwell 1971). Even in laboratory experiments, it has been shown that oil which was mechanically emulsified by a homogenizer was far more toxic than oil that was manually mixed or stirred by aeration (Tarzwell 1971). This may partially be due to the fact that oil treated with surfactants is more likely to cross skin and internal membrane barriers.

The potential for toxic synergism between surfactants and crude oil is an important issue. Mixing dispersants with spilled oil to facilitate its cleanup and the use of surfactants to help extract it pose serious threats to aquatic systems. It is reported that, when dispersants were mixed with crude oil, the differences (or spread) in toxicity of different dispersants to test organisms rose 187-fold (Tarzwell 1971). Mixing crude oil with these compounds, which are often used to help mitigate the ecological effects of an aquatic spill, greatly increases the toxic effects on organisms such as fish by emulsifying and spreading crude petroleum constituents throughout the water column. The effects of such compounds were included above in Table 3.

Compounds such as surfactants are not only found mixed with water and crude petroleum in the event of a spill, but they are also used as an aid in producing crude oil in some tertiary recovery processes. Surfactants used for this purpose are involved with the formation of oil micro-emulsions within the oil reservoir. The formation of such oil-surfactant emulsions helps solubilize the crude petroleum, facilitating its movement to the earth's surface. In addition to any direct toxicities that the various surfactants used in crude production have, they may facilitate the process of solubilizing toxic components present within the crude oil, making them more "available" to aquatic organisms, e.g., by easing their penetration through epithelial barriers (Schumacher 1978). In effect, crude oil in a freshwater system may have different degrees of toxicity depending on the process used to extract it, especially if a particular extraction technology uses compounds that could intensify the normal effects of the crude oil.

Bioassay Testing

In addition to synergistic reactions between crude oil and production-associated components, it is also important to consider the effects of individual compounds occurring naturally in crude oil. Obtaining meaningful acute toxicity values for crude oil in laboratory procedures such as the 96-hour LC50 test, and for oil spills in the field is impossible without characterizing the specific petroleum compound. This is due to the large number of components present in crude oil (U.S. Environmental Protection Agency 1976). There is no "average" crude oil in regard to the concentration or proportion of the materials it contains. For this reason, individual chemicals and combinations of constituents of petroleum should be tested for both lethal and sublethal effects.

Sublethal Effects

In addition to the more prevalent studies on acute toxic effects, some data on sublethal effects of petroleum and associated compounds on freshwater compounds are available. Sublethal effects include those which may not cause immediate death, but result in disruptions at the biochemical level or produce disruptions in normal feeding, reproductive, or behavioral patterns. It has been reported that sublethal effects from concentrations of crude oil as low as 10 to 100 ug per liter can disrupt the normal behavior of various types of aquatic life (U.S. Environmental Protection Agency 1976). With experiments utilizing salmon fry, the response varied with the size of the fry. Small fry were found to be far more tolerant to crude oil than were larger fry at concentrations of less than 2 ppm (Rice 1973). It has been postulated that avoidance reactions might have a disruptive effect on the migratory patterns of these fish. Such an effect could be extremely severe in the smaller rivers and creeks in which these fish originate and to which they must return to spawn.

Effects of Benzene

As mentioned earlier, benzene constitutes 20 percent or more of the total aromatic constituents in oil, and it has a high degree of water solubility (Brockson and Bailey 1973). Tests on this compound with juvenile Chinook salmon indicate that benzene can have a profound effect on respiration. Juvenile salmon were exposed to concentrations of benzene equivalent to 5 and 10 ppm over a total time period of 96 hours. Measurements of respiration were taken at 24, 48, 76, and 96 hours. It was found that exposure to 5 ppm caused an increase in the rates of respiration irrespective of the length of exposure time. However, the magnitude of the increase was related to length of exposure time, with the greatest percentage increase (86 percent) after 48 hours and less pronounced effects at 72 and 96 hours. The same relationship was found to exist at 10 ppm as at 5 ppm, with respiration rates increasing at every exposure period except 96 hours. The investigators noted that the mean increase in respiration rate for fish exposed to 10 ppm benzene for 48 hours was 115 percent (Brockson and Bailey 1973). Narcosis was another effect noted for fish exposed to 10 ppm benzene for longer time periods than described. This effect was accompanied by decreases in respiratory rate, and was found to be reversible when the animals were placed in fresh uncontaminated water. Similar increases in ventilation rates were observed in a series of diurnal tests using various surfactants (Maki 1979).

Detoxification and Bioaccumulation

Another area which may have far reaching implications for freshwater organisms involves a specific metabolic response on the part of some organisms to the presence of petroleum or its constituents. Exposure to petroleum or benzo(a)pyrene activates an aryl hydrocarbon hydroxylase (AHH) enzyme system in various species of freshwater trout (Pedersen et al. 1978; Ahokas et al. 1974; Payne and Penrose 1975). This enzyme system appears to function as a detoxification mechanism in some species of freshwater fish (Payne and Penrose 1975).

The ecological and health significance of this pollution induced enzyme system may be great. It has been suggested that the catabolic intermediates of these detoxification reactions may produce metabolites that are more toxic than the compounds upon which they initially act (Rice et al. 1976). Whether the effect of induction is on the activation or the detoxification of carcinogenic polycyclic aromatic compounds within petroleum remains to be fully elucidated (Payne and Penrose 1975). What has been demonstrated is that some aquatic organisms have the ability for pollutant biotransformation. Both experiments and field observations (Payne and Penrose 1975) using brown trout have demonstrated the induction of this biochemical mechanism. Fish were taken from two lakes, one clean and the other polluted with oil. In laboratory experiments, fish from the clean lake were placed in large recirculating tanks to which small amounts of a homogenized crude oil-water mixture were added. At the same time, in field experiments, fish were taken from both the polluted and a clean lake for comparative purposes.

Fish from the clean lake that were exposed to oil in the laboratory showed significant increases in AHH activity within 17 days. There was also a significant difference between the gill activity of exposed fish and controls. There was, however, no noticeable difference in mortality or behavior between the exposed fish and the controls (Payne and Penrose 1975). Fish taken from the clean and polluted lakes displayed significant differences in AHH activity, with fish from the polluted lake not only having significantly higher levels of activity, but also maintaining those levels over a period of 1 year in captivity.

Other investigations of petroleum constituents have focused on uptake, bioaccumulation, and rates of excretion. In this context, Melancon and Lech (1979) studied two ^{14}C -labeled constituents of crude petroleum that are highly water soluble and that accumulate in some marine invertebrates. The compounds examined were ^{14}C -labeled naphthalene and ^{14}C -labeled 2-methylnaphthalene. The experimental fish were rainbow trout, carp, bluegill sunfish, and a marine

species. The uptake and subsequent elimination of these compounds were examined after both short-term (8- or 24-hour) and long-term (4-week) exposure periods.

Rainbow trout exposed to ^{14}C -labeled naphthalene rapidly accumulated it, but at the end of 24 hours, only 4 percent remained in the muscle tissue. When the trout were exposed to this compound for 4 weeks, the tissue levels rose slowly and were eliminated slowly over an ensuing 5-week period. Trout exposed to ^{14}C -2-methylnaphthalene for a 4-week period showed a similar uptake pattern, but a different elimination pattern than with naphthalene. It was found that elimination of the 2-methylnaphthalene was a biphasic process, i.e., there was an initial rapid phase of elimination that had a half-life of less than 24 hours, and also a slow phase that had a half-life of hundreds of hours. Experiments with carp and bluegill sunfish exposed to this same compound for 4 weeks also exhibited a biphasic elimination pattern. Examination of muscle taken from the trout suggested that the difference in elimination rates (steady versus biphasic) for these compounds may depend on whether the compounds were accumulated and stored by the tissues as the parent compounds or as their metabolites. In this context, experiments were carried out by pretreating trout with B-naphthoflavone before they were exposed to either of the ^{14}C -labeled compounds. The treated fish had a greater proportion of ^{14}C catalytic metabolites than did controls.

Plankton

The effects of petroleum have been studied not only with fish, but also with freshwater plankton and benthos. Information on these latter groups is extremely limited, however, especially when compared to field and laboratory investigations on marine and estuarine species.

Field studies on freshwater plankton have focused on petroleum's effects on gross population trends and on the chemical characteristics that help regulate populations. McCauley (1966) investigated the effects of a petroleum spill on river biota and associated chemical parameters. In the area of the spill there was an initial decline in the amount of dissolved oxygen found that was attributed to a partial exclusion of atmospheric oxygen caused by the oil film. This film gradually dissipated with time, with much of it being adsorbed onto suspended matter, including petroleum-killed plankton. The material subsequently sank to the river bottom, forming an oily sludge in the sediment. Both high nitrate and phosphate levels were found. These nutrient levels were attributed to bacterial decomposition of plankton killed by the petroleum. Although limited in species diversity, large differences in abundance were found for the

zooplankton present. Some of this abnormal variation was correlated with the oil pollution. The major observation noted with the planktonic algae was that a spectrum of petroleum sensitivity existed; some groups tolerated the presence of oil during the entire 2-year study, while other groups were eliminated. Among the major freshwater algae found to be highly tolerant of the oil were species of Lyngbya, Oscillatoria, Euglena, and Scenedesmus.

In experiments using freshwater algae taken from lakes high in nickel (a major petroleum trace metal), the algae, rather than fish, were adversely affected. In other experiments, a major species of freshwater algae (Scenedesmus) was cultured from a lake that contained varying amounts of both copper and nickel. This particular organism was described as relatively metal tolerant. Experiments were conducted to determine if potential interactions might exist between these two metals, and how they might affect the algae. It was found that nickel alone was far less toxic than copper alone. However, even when low amounts of nickel were present together with low amounts of copper, toxicity was greatly increased (Stokes and Hutchinson 1976). The toxicity was not due to nickel, but was characterized as resulting from the copper. Evidently, the nickel, even in very small amounts, initiated a synergistic reaction that resulted in large amounts of copper being assimilated by the algae (Stokes and Hutchinson 1976).

Research dealing with effects of the more prevalent organic compounds in crude oil also has yielded data of potential significance to freshwater ecosystems. Hutchinson et al. (1980) examined the possible correlation between physical and chemical properties of various organics and their toxicity to two representative freshwater algae: Chlorella vulgaris and Clamydomonas angulosa. Among the compounds examined were members of various straight and branched chain alkanes, cyclo-alkanes, aromatics, and polynuclear aromatics. Toxicity was measured as the concentration of a compound necessary to cause a 50 percent reduction in algal photosynthesis. The characteristics examined were solubility and the octanol-water partition coefficient. A wide range of water solubilities existed among the tested organics. Solubilities extended over eight orders of magnitude. The range in octanol-water partition coefficients was almost as great, extending over six orders of magnitude. Test results for compounds in various organic classes showed a strong correlation between the degree of algal toxicity and the solubility and octanol-water partition coefficients of the 38 compounds tested. The toxicity to algae from representative compounds in various organic classes were shown in Table 3. Algal toxicity increased with the solubility of the pollutant, but hydrocarbons with a low solubility were generally more toxic (on a molar basis) than were high solubility compounds such as benzene (Hutchinson et al. 1980).

Benthic Organisms

Limited data are available on the effects of petroleum and its constituents on freshwater benthos. McCauley (1966) examined the effects of a petroleum spill on both algal and benthic organisms in a freshwater river.* In the latter group, much the same situation was found to exist with benthic organisms as with planktonic algae, i.e., some groups were extremely tolerant of oil and others quite sensitive. Nematodes appeared to be highly tolerant of the petroleum. As many as 20 genera were identified in the worst area of pollution, and these thrived even when the pollution was at its maximum. Other organisms varied in their response, with "clean water" species such as Dugesia (a flatworm) being eliminated and forms such as Tubifex (an annelid worm) being very tolerant. This same pattern was seen for other benthic groups such as Crustacea and Hirudinea (leaches).

Another study (Kalas et al. 1980) examined the bioaccumulation potential for polynuclear aromatic hydrocarbons by a major and widespread benthic gastropod: Cipangopaludina chinensis. This organism has a long (6- to 15-year) life span, and during the winter it hibernates in pond and river sediments. Its intimate mode of existence on and in sediment, along with its widespread distribution, makes it a good indicator of specific types of pollution. In this study, both sediment and snails were compared for their concentrations of 18 different polycyclic aromatic hydrocarbons. Of these 18 compounds, 4 were below the detection limit in the snails, but were found to be present in the sediment. With one exception, all of the remaining compounds were present at higher levels in the snail than in the sediment. The levels found in the snails were from 15 to 200 times those found in the sediment. These data suggest that some freshwater benthic organisms that are exposed to oil-contaminated sediment may concentrate some compounds far in excess of the levels found in the medium in which they exist.

Terrestrial Biota

In the Onshore section of this report, discussion of ecological effects has focused on the freshwater aquatic biota, which are more likely to be impacted by drilling activity than terrestrial biota.

An extensive discussion of the effects of spilled oil and air emissions from oil and gas activities on terrestrial biota is contained in the Transportation and Storage section. The transportation facet of the oil and gas industry threatens terrestrial biota with potential oil spills.

*In this study, oil reached the bottom organisms in the form of an oily sludge.

Summary of Research Needs

Knowledge of the effects of onshore petroleum production on freshwater biota covers a broad spectrum and is in-depth, as indicated in the above discussion. Water discharges from onshore drilling rigs are controlled and drilling mud wastes are recycled or disposed of in waste pits.

Research has focused within the last decade on developing procedures for dealing with spills. The U.S. Environmental Protection Agency (and the U.S. Coast Guard in near shore waters) is responding to accidental and intentional discharges and has developed measures for the control, removal, and safe disposal of these spills. Technology for detection, control, and removal is under development at the Industrial Environmental Research Laboratory's Oil and Hazardous Materials Spills Laboratory in Edison, New Jersey.

Thus, the focus of Federal research on freshwater oil spills has shifted from effects to the development of control strategies. Effects research is largely centered in academic institutions and focuses on basic research problems.

TRANSPORT AND TRANSFORMATION

This section describes the movement and possible transformations in air and water media of pollutants that may be associated with petroleum production. A pollutant is considered to be any element or compound used in or produced by petroleum technologies that has or may have adverse effects on human health or the environment.

Water Medium

In primary and secondary petroleum production, large amounts of brine are associated with the produced oil. It has been estimated that 30 million barrels of such brine are produced daily in the U.S. (Meier 1978). After separation from the oil, this brine must be disposed of in some manner. The amount of brine and the manner of disposal may have a direct bearing on the movement of the brine (and other pollutants associated with it) into undesirable locations such as groundwater.

Brines associated with oil production are usually reinjected into the earth for one of two purposes: disposal or to increase oil production, e.g., by waterflooding (U.S. Environmental Protection Agency 1977). When brine is reintroduced into the earth for disposal, it is often injected into deep saline aquifers through abandoned production wells, or it may be reinjected directly into the stratum of the oil formation from which it was withdrawn (U.S. Environmental Protection Agency 1977). When brine is disposed of through wells that use injection techniques, especially if these wells are older production wells, there is the possibility of contaminating freshwater aquifers. These older production wells may be poorly designed for use as waste injection systems. Also, ruptured or corroded casings may allow the movement of brine into freshwater strata (U.S. Environmental Protection Agency 1977).

The industry makes an effort to prevent brine transport into freshwater strata when drilling or chemical waste injection procedures are begun. Engineering and design specifications to prevent such occurrences may be quite varied, but certain procedures are common among many extraction techniques. In any initial drilling operation, various types of geological strata are penetrated. Each strata may contain salt water, fresh water, gas, oil, or a mixture of gas, oil, and water. Both casings and extensive use of cement are employed to prevent brine transport between these strata. Each of the various geological strata above the oil or gas producing zone is cased and cemented to prevent such movement from occurring (Meier 1978). The actual surface casing string is set and cemented from 30 to 100 feet below the deepest freshwater layer that is capable of self-replenishment and which could be used for various human

activities (Meier 1978). Unfortunately, even with elaborate precautions, movement of pollutants, such as brine from saline strata, into freshwater zones can occur. Such pollutant movement may be from breaks or leaks in casing strings or associated structures. These, in turn, may be the result of such diverse causes as natural fault movement and subsidence or corroded and improperly plugged wells (Schumacher 1978). Pollution transport also may come about as a result of induced changes within the natural formation itself, resulting from oil recovery or waste disposal practices. For example, pressure is required to inject fluids or gases into the oil or gas formation in various enhanced recovery techniques. Pressure is also employed to inject brines and other chemical wastes into disposal wells. Injection pressure from either of the above causes can lead to fissures being created within the formation (Schumacher 1978). Such fissures could allow for movement of the brine or chemical wastes from saltwater strata into freshwater strata located within the same formation.

Other means by which brines, expended drilling muds, and cuttings may contaminate groundwater supplies are through surface waste disposal pits. These pits may be lined or unlined. Loss of the integrity of these pits occurs. Sometimes spills occur due to flooding and embankment failure. If surface leakage is indicated, various impervious materials such as gel, polymer, or plastics may be used to prevent leakage (Meier 1978). If brines, expended muds, or cuttings are placed in unlined waste pits, the real possibility of transport to groundwater and subsequent contamination must then be considered. It should be emphasized that large amounts of cuttings are associated with drilling a well, and these cuttings may be contaminated with organics both from the oil-containing formation itself and from drilling fluids (Wilkins 1977). The types of chemicals used in formulating drilling fluids (muds) are large in number and contain many, varied types of inorganic and organic compounds. The ingredients have been variously listed as including everything from pH-control products, bactericides, calcium-removers, corrosion inhibitors, defoamers, emulsifiers, filtrate reducers, flocculants, foaming agents, lost circulation materials, lubricants, shale-control inhibitors, surface-active agents, thinners, dispersants, and viscosifiers, to weighting agents (Richards 1979).

Mud and brine pits are often bulldozed flat following evaporation and abandonment. As a long-term source of undesirable leachates, the discarded saline mud poses environmental problems with respect to land reclamation and agricultural use.

In general, there is little information available on the specifics of any reservoir transformation reactions occurring with chemicals that are initially injected into a formation. Since it is

possible for various compounds in the oil formation to move into freshwater aquifers, the potential exists for these original chemicals to be transformed within the formation, creating a toxic "reservoir" if released to external water supplies. This potential should be examined and there should be consideration of some of the potential mechanics of transformation that may occur once these, or other pollutants, actually reach aquatic systems.

Surfactants constitute a large group of chemicals widely used in oil extraction techniques. The surfactants that are frequently used are composed of long chain alkyl- and aryl-sulfonates (Schumacher 1978). Many of these compounds are produced by a reaction requiring sulfonation. It has been reported that the sulfonation reaction is reversible and many compounds are sulfonated on site (Schumacher 1978). The stability of these, and perhaps other commonly used compounds, may thus be compromised under various conditions of reservoir temperature, pH, and pressure.

Once pollutants have entered an aquatic system, they are subject to a large number of chemical transformations. The pollutants themselves or the chemical agents with which they react may be elemental, e.g., metals; inorganic or organic compounds, or ions. In addition to considering the movement of these pollutants, there is a concomitant need to analyze factors that may affect their transformation from one physical or chemical state into another. Among such factors are temperature, pH, pressure, oxidation-reduction potential (redox), hydrolysis reactions, adsorption, and absorption.

One of the most important factors affecting pollutant transformations is the oxidation-reduction potential of the aquatic environment in which the pollutant is found (Tinsley 1979). This, in turn, is affected by the pH of the aquatic medium. Chemical reactions take place when electrons are lost from one compound or chemical species and gained by another. These are termed oxidation-reduction reactions and any system in which these reactions occur may be termed a redox system or environment. Water is a redox environment. The loss or gain of electrons by a pollutant in such an environment is important because, once a pollutant has become transformed (oxidized or reduced), it can possess radically different properties (Tinsley 1979). The change in properties may also change the biological and environmental effects of the pollutant. It is important to note that different types of aquatic systems differ greatly in their relative oxidizing or reducing capacity. The same pollutant entering a stagnant lake may produce pollution degradation products quite different from those produced when it enters groundwater.

The chemical behavior of a toxic metal in water demonstrates redox effects on toxicity. Mercury, a toxic metal, may exist under certain aquatic (redox) conditions in the form of a positive ion (differing in chemistry and appearance from the common silvery metal). Under these conditions, this electrically positive ion of mercury may chemically join with many types of electrically negative ions to form any number of different compounds, or it may be ingested by microorganisms to form a methyl mercury complex (Tinsley 1979). (Methyl mercury is several times more toxic than metallic mercury.) Should the redox of this aquatic system change, that same initial positively charged ion of mercury could be converted into a thin film of the common metal and be volatilized from the water.

Organic compounds also may be directly affected by changes in aquatic redox systems. Unfortunately, these are not well characterized. It has been shown, however, that organic compounds do undergo chemical changes associated with the redox state of the water. This has been demonstrated for some of the chlorinated hydrocarbons, such as toxaphene and DDT. In the latter case, redox changes that favor the formation of a specific ionic form of iron greatly increase the conversion of DDT to DDD (Tinsley 1979).

Also of importance in the transformation and/or degradation of organic or inorganic compounds in aquatic systems are hydrolysis reactions (Tinsley 1979), i.e., direct reactions with water by various compounds, or the potential for these compounds to react with water. The study of hydrolysis reactions encompasses a huge body of chemical literature. A brief survey of a few of the important classes of compounds that can be affected by hydrolysis may provide a perspective on the importance of this kind of reaction in the transformation of aquatic pollutants.

Esters, amides, carbamates, organophosphates, and various halogenated carbon compounds are representative of major classes of organic groups. Esters and the halogenated hydrocarbons encompass large numbers of compounds used or produced in petroleum operations. These two groups can be used to illustrate some of the factors affecting hydrolysis. An ester is the product of a reaction between an alcohol and an organic carboxylic acid. A halogenated hydrocarbon compound contains one or more of the halogen elements (I, F, Cl, Br).

Esters may be hydrolyzed by three different mechanisms that are termed acid catalyzed, base catalyzed, or neutral. These mechanisms, the rates of formation, and the amounts and types of degradation products that are formed may be affected by the pH of water, which can be altered by a spill. In addition to pH, the position of various chemical groups attached to the ester molecule will also affect the compound's rate of degradation (Tinsley 1979).

The halogenated hydrocarbons are also of interest due to the large number of these compounds that are in use. Like esters (some of which also are halogenated), these carbon compounds display a wide variety of characteristics that may affect their aquatic transformation. In some of these compounds, e.g., the chlorinated methanes, the rate of hydrolysis decreases as additional chlorine atoms are added to the compound. Furthermore, it is known that great variations exist in the rate of hydrolysis for these compounds with some, such as the chlorinated benzenes, being quite resistant to hydrolytic transformation (Tinsley 1979).

Chemical redox and hydrolysis reactions are major, but not the only determinants in aquatic pollutant transformations. Physical (adsorptive) phenomena also can occur. This may involve the adsorption of elements (e.g. metal ions onto aqueous sediment or various chemical compounds onto dissolved particulate matter). Adsorption is a complex phenomenon and most experimental work has been done on inorganic systems for which models have been developed. For example, one of the single most important parameters affecting a metal's adsorbability appears to be pH. There appears to be a specific, and often narrow pH range for every metal over which that metal will be completely adsorbed and removed from solution (Leckie and James 1976).

The behavior of aquatic organics is poorly understood and much remains to be clarified.

Air Medium

Airborne pollutants associated with onshore production are not unique to the oil and gas industry. A discussion of common transport, transformation, and fate problems, as well as research needs, is provided in the Basic Effects Issues section of this report.

Summary of Research Needs

Some research needs related to the general impacts of oil and gas activity on water quality are presented in the Basic Effects Issues section. Research needs that specifically concern onshore oil and gas production are discussed below.

Oil and gas development has been excluded from many controls applicable to other industries, such as provisions under the Safe Drinking Water Act intended to assure groundwater protection, despite the fact that petroleum can enter potable aquifers through cracks and fissures in strata adjacent to oil wells where spills or leaks may occur. Traditionally, taste and smell have been used to detect petroleum in water. However, many of the more toxic and

carcinogenic components of crude oil have no detectable odor or taste at potentially toxic concentrations. This factor, and the use of bactericides, pH-control substances, calcium-removers, defoamers, and emulsifiers require the development and use of sophisticated sampling and measurement devices to routinely detect these substances in ground and surface water.

The stability of surfactants, especially with respect to the reversibility of the sulfonation of surfactants, should be investigated. The conditions of reservoir and aquifer temperature, pH, and pressure which affect the reactions should be studied.

The state of the art of tracking the movement of pollutants through groundwater systems is at an early stage of development. Dyes, Lycopodium spores, and other techniques have been used to trace and detect contamination of groundwater. With respect to the field production of oil and gas, methods should be developed, including indicator "tracers," which can be used to detect and trace pollutants associated with onshore production through groundwater aquifer systems.

Many petroleum-related pollutants may undergo chemical transformation in the environment. These transformations and the toxic effects of their products require study to aid hazard assessments of the new and chemically complex extraction technologies.

Part 3

Offshore Development

OFFSHORE SUMMARY

This section observes that, with offshore oil and gas development, there is a need for adequate data reporting. Data on injuries, illnesses, and fatalities for onshore and offshore drilling rigs have been commingled. Onshore and offshore activities have diverged markedly over the last decade, leading to substantial differences with respect to the nature and extent of risks. A more appropriate and effective information gathering and reporting system should be developed.

A number of tragic offshore drilling and production rig accidents have recently focused attention on the need for greater understanding of the causal factors and potential mitigating measures which may be taken. A number of needed research and data collection activities are cited in this section.

Research is needed to define offshore oil and gas worker exposures and potential health risks related to the handling of the various formulations of drilling muds. The findings would also be applicable to onshore production. Retrospective epidemiological surveys, possibly focused on workers in the Gulf Coast Basin would be useful in understanding the extent of this potential health problem.

The trend toward the greater use of offshore oil and gas transfer, loading, storage, and processing facilities may pose a significant problem with respect to air pollution. The effect of these airborne emissions and possible transformation reactions should be explored.

With respect to environmental effects, additional research is needed on the long-term effects associated with the release of drilling fluids in the marine environment, especially as a result of continuous loading within a developing field. Several research areas associated with this subject (e.g., entrapment in trenches, effects of degradation products, effects in high energy environments) require clarification.

Research is also needed on the effects of exploratory techniques. During exploratory surveys in hostile environments, such as in the Beaufort Sea, a large seismic shock from the detonation of powerful explosives may be more desirable than repeated low-energy intensive shocks. The single, larger shock may have less impact on marine biota. Additional information is needed in this area to establish guidelines for exploratory activity in hostile marine environments.

To date, oil and gas environmental studies have focused on the shallow waters of the continental shelf. With the use of modern mobile rigs and subsea completion systems, the deep ocean floor of the continental shelf, its trenches, and the continental slope can be exploited. The impact of such activity on this relatively stable environment and sensitive biota should be explored.

Many impacts have been postulated to occur as a result of chronic hydrocarbon discharges into the marine environment. The cumulative impacts of such discharges should be studied through the use of natural seeps as sources of oil discharges.

Specific research needs associated with the above mentioned problems can be found within the Summary of Research Needs sections. Discussion of the respective health and environmental problems may be found in sections preceding the research needs summaries.

OFFSHORE OIL AND GAS PRODUCTION

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OFFSHORE OIL AND GAS PRODUCTION

TECHNOLOGY DESCRIPTION

Exploration

Exploratory activities are undertaken to locate geological formations which may contain oil and gas accumulations. These activities usually progress through the following principal phases (Kash et al. 1973; University of Oklahoma 1975):

- o Regional surveys to identify promising geological formations;
- o Detailed surveys on which evaluations of specific areas are based; and
- o Exploratory drilling to determine whether oil and gas are actually present in a given area.

Exploratory Surveys

Regional surveys involve passive reconnaissance techniques similar to those used for land exploration. Air and shipborne measurements are made of variations in the earth's magnetic and gravitational fields. Regional surveys are also conducted to detect natural seeps of hydrocarbons into the atmosphere. If the results of these passive reconnaissance techniques are promising, then more detailed, active surveying techniques such as seismic analysis, bottom sampling, and coring are usually conducted.

Seismic surveying involves using an energy source to generate sound waves which are reflected and refracted from subsea geological formations (Figure 1). The sound waves are picked up by hydrophones suspended from the research vessel. In the past, explosives were used to generate the sound waves; however, due to resulting adverse environmental impacts and the practicality of new techniques, the use of explosives has been replaced with alternate energy sources (Kash et al. 1973). Currently, contained detonations of a propane and oxygen mixture or high-powered oscillators are used to generate the sound waves.

Other active surveying techniques involve taking samples of the ocean floor and coring to obtain subsurface samples for geological examination. These geophysical survey techniques and geological studies are useful to identify areas in which oil and gas may be found; however, exploratory drilling is necessary to determine whether commercial quantities of oil and gas are present.

FIGURE 1
SEISMIC OPERATIONS

Exploratory Drilling

The major difference between offshore exploratory drilling operations and those on land is that, offshore, a support system for the drilling rig and associated equipment is needed. Fixed platforms, due to their expense and the difficulty associated with moving them, are used primarily for production purposes (Clark et al. 1978). Four kinds of mobile platforms usually are used for offshore exploratory drilling: barges, drill ships, jack-ups, and semisubmersibles.

Barges are not self-propelled and must be towed from one drilling location to another (Harris 1972). Because of their lack of seaworthiness, barges are normally used in shallow, protected waters, although some have been built for drilling in water depths as great as 600 feet (University of Oklahoma 1975).

Drill ships, on the other hand, are self-propelled and are often used to drill in waters from 500 feet to 3,000 feet in depth (Council on Environmental Quality 1974). These vessels maintain their position over a well site by using either anchors or dynamic positioning propellers to compensate for movement (Figure 2). Drill ships may not be suitable for severe weather (University of Oklahoma 1975); however, modern drill ships (e.g., Glomar 40) are designed to maintain operations in winds of 60 miles per hour and waves of 50 feet (Clark et al. 1978).

A jack-up, or self-elevating drilling platform, has buoyant hulls that enable the rig to be towed to the drilling site (Figure 3). Upon reaching the drilling site, the legs, which are fitted vertically through slots in the hull, are lowered either mechanically or hydraulically until they reach the ocean floor. The platform is then raised or "jacked-up" above the ocean surface until it is elevated above the height of anticipated waves. Jack-ups are extremely stable and provide a secure drilling position when used in the appropriate depths (Clark et al. 1978). They are designed to withstand severe weather conditions in shallow water, and under calm conditions they can operate in depths up to 300 feet.

The semisubmersible (Figure 4), the newest type of drilling rig available, has excellent stability in severe weather and can drill in water as deep as 2,000 feet (Kash et al. 1973; University of Oklahoma 1975). The platform deck may be supported by columns connected to large underwater displacement hulls, mounted on large vertical caissons, or supported by some combination of the two (Harris 1972). A semisubmersible may be self-propelled or towed. When it reaches the drilling site, the columns, displacement hulls, or caissons are flooded, which reduces wave forces by locating the major buoyancy members (and the wave action) beneath the surface (Harris 1972).

FIGURE 2
POSITIONING OF DEEP WATER DRILL SHIP

FIGURE 3
JACK-UP DRILLING RIG

FIGURE 4
SEMISUBMERSIBLE DRILLING RIG

Like drillships, semisubmersibles maintain their location with either anchors or a dynamic positioning system.

Jack-ups and semisubmersibles are most widely used for offshore exploratory drilling operations. A recent survey of the world's mobile drilling rig fleet listed 271 jack-ups, 123 semisubmersibles, and 88 drillships and barges (Tubb 1979).

Once the platform is positioned over the drill site, the drill stem is lowered to the ocean floor through a conductor pipe or a marine riser (Figure 5). The methods and equipment used for offshore drilling are very similar to those used on land. Most wells, whether offshore or onshore, are drilled by rotary drilling methods which utilize (Sittig 1978):

- o Machinery to turn the bit, to add sections on the drill pipe (i.e., drill string) as the hole deepens, and to remove the drill pipe and the bit from the hole; and
- o A system for circulating a fluid (i.e., drilling mud) down through the drill pipe and back up to the surface.

The well bore is drilled by rotating the drill bit which is on the end of the string of drill pipe. Drilling mud is an important component of a drilling operation. It removes particles cut by the bit, cools and lubricates the bit, stabilizes the walls of the well bore, and controls any pressures that the bit may encounter in its passage through various formations (Sittig 1978).

The drilling fluids that are discharged within the marine environment are typically water-based slurries containing clays and various chemical and mineral additives. Federal regulations prohibit the discharge of oil-based and oil-emulsion fluids. The specific formulations used in oil and gas exploration activities vary widely, although most contain barite (barium sulfate) for density control and low concentrations of sodium hydroxide, chrome lignosulfate, lignite, and other chemicals to control viscosity, fluid loss, corrosion, and other mud properties (Ayers 1980a; Petroleum Equipment Suppliers Association 1980).

These materials are released at drilling rig platforms both as relatively small-volume operational discharges and as infrequent large-volume bulk discharges. It is estimated that a total of 10,000 to 30,000 barrels of mud, containing 20 to 30 percent solids, is discharged over the life of a typical well (Ayers 1980a). From about 1,500 new wells drilled in U.S. offshore waters in 1979 (U.S. Geological Survey 1980), it is estimated that 15 million to 46 million barrels of drilling fluid were discharged into the marine environment.

FIGURE 5
FLOATING DRILLING SYSTEM

More than 90 percent of this activity occurred within the Louisiana and Texas lease sale areas.

Exploratory drilling is one of the most hazardous steps in the development of offshore oil and gas reserves due to the possibility of a blowout--the sudden surge of oil or gas pressure up the drill hole causing loss of control over the well (Council on Environmental Quality 1974). In addition to the drilling mud, safeguards used to minimize the possibility of a blowout include the setting of casing and installation of blowout preventers.

The casing usually consists of relatively large-diameter steel pipe and is used to line the bore hole (Kash et al. 1973). The type of casing used depends on the geological structures and pressures encountered during drilling. The surface casing provides an attachment site for the blowout preventer stack, which is a series of control valves that can close part or all of the drill hole in case of a blowout.

Development Drilling and Well Completion

Development Drilling

If exploratory drilling reveals commercially exploitable quantities of oil and gas, then preparations may be undertaken to begin production. Production operations are initiated by installing a platform to serve as a base for drilling development wells (Figure 6). In contrast to exploratory drilling, most offshore development drilling and production facilities utilize fixed platforms.

In shallow waters, platforms are usually constructed by first driving pilings of wood, steel, or concrete into the ocean floor and then constructing the platform or installing a prefabricated platform on the pilings. In deeper waters, the platform is prefabricated onshore, floated or barged to the location, and sunk in place.

Platforms are not standardized, but are designed for each specific location. Components such as motors, derricks, cranes, and housing modules are standard items, but the structure on which they are housed may stand in waters ranging from 50 to 1,000 feet deep. Factors such as depth, sea floor soil conditions, wave action, winds, sea floor stability, and the weight of the structure must be considered (Clark et al. 1978). Platforms may be designed only for drilling and workover, or for a combination of drilling and production. Subsequent to drilling, some platforms may be converted to housing and recreational areas for field personnel. Many of the fields in the Gulf of Mexico and in the North Sea use a drilling platform for the development wells and a satellite platform for the production

FIGURE 6
FIXED-PILE (PRODUCTION DRILLING) PLATFORM

facilities. In deeper waters, the trend is toward combining platform functions since costs increase greatly with depth (U.S. Geological Survey 1976).

An emerging alternative to fixed production platforms is the subsea production system which involves placing the wellheads on the ocean floor rather than on platforms (Figure 7). The produced liquids or gases are transferred from the wellhead either to a nearby fixed platform or to a shore facility for processing (Kash et al. 1973). The subsea production systems exist in a variety of configurations, including: wet systems, in which the wellhead equipment is exposed to water; and dry systems which contain essentially conventional wellhead equipment within watertight chambers maintained at atmospheric pressure (Kash et al. 1973). However, there are three basic types of subsea systems under development: single subsea wells, encapsulated systems, and nonencapsulated multiwell systems. The encapsulated system involves the use of dry chambers to enclose dryland wellheads on the ocean floor. Workmen enter the one-atmosphere pressure chamber from a diving bell or submarine. The single subsea well and the nonencapsulated multiwell systems are both wet systems. Production equipment for the nonencapsulated multiwell system is located within the system and is serviced by a diving bell that can be either manned or unmanned (Kash et al. 1973; Council on Environmental Quality 1974).

Economic advantages that favor the increased use of subsea production systems are (Ocean Industry 1978):

- o Establishment of early production. The construction of an offshore platform and wells may take 5 years, whereas subsea systems can be completed within 1 year. This allows for early evaluation of a reservoir's production before heavy investments are made in permanent structures and provides an early cash flow supply.
- o Utilization of exploratory wells as production units. Seafloor completions can be used to tap exploratory wells that are ordinarily plugged. These units can be tied to a platform for operating.
- o Recovery and reuse of equipment. In contrast to platforms, subsea equipment can be inexpensively recovered after production is terminated.
- o Production from marginal fields. The low cost of subsea systems permits their use in fields that would normally be abandoned due to low yields.

FIGURE 7
SUBSEA PRODUCTION SYSTEM

- o Complete field use. Subsea systems can be used to tap areas where overburden is shallow and to service outer areas of a reservoir that cannot be reached with platform development wells.
- o Deepwater production. A goal of the developers of subsea systems is to design equipment to operate at water depths below the economic operating depths of conventional platforms. Some subsea systems can be successfully installed and operated in water depths up to 3,000 feet.
- o Unstable seafloors. Subsea systems can operate on sediments that cannot support a production platform.
- o Avoidance of ice. Platforms erected through the air-sea interface in arctic regions may be damaged by wind and current-driven sheet ice and icebergs.

After the fixed platform or subsea system is assembled, development drilling, similar to exploratory drilling, commences. Development wells can be drilled vertically and individually, like exploratory wells, or they can be drilled directionally to cluster the wellheads in one location. With the latter method, the drill is directed off a vertical line to reach lateral sections of the oil or gas reservoir, making the most economical use of expensive platform space (Figure 8). Directional drilling requires the use of special production rigs (mounted on the platform) which can rotate the drill strings through the drive or conductor pipe that may be set at an angle of up to 30° with the ocean floor. Modern platforms accommodate as many as 60 wells (Clark et al. 1978).

The drilling procedures for development (production) wells are essentially identical to those for exploratory wells (Kash et al. 1973; U.S. Geological Survey 1976). Alternatives to the rotary drilling process are being examined and include the use of a flexible drill string, a jetted particle system, high fluid pressure drilling, and explosives.

Development drilling is generally less hazardous than exploratory drilling because the characteristics of the geological formations are better known. However, there is still the potential threat of a blowout. The severity of a development well blowout increases significantly if oil and gas are being produced simultaneously from wells that have already been completed (Council on Environmental Quality 1974).

FIGURE 8
TYPICAL DIRECTIONALLY DRILLED WELLS

Well Completion

If a well is dry, it is plugged with cement and abandoned. If commercial quantities of oil or gas are found, the well is "completed"--a term that refers to the various activities required to transform a well into a producer of oil or gas. Kash et al. (1973) have described completion as incorporating the following activities:

- o Setting and cementing casing;
- o Perforating, or cutting holes in the casing that will permit oil or gas to flow from the formation into the well hole;
- o Fracturing, or applying pressure or using explosives to increase permeability;
- o Acidizing, or using acid to enlarge openings in the formation;
- o Consolidating sand to keep sand from filling the well bore;
- o Setting tubing, or a conduit for routing the oil or gas to the surface; and
- o Installing downhole safety devices, or valves to prevent blowouts during production.

If any of these activities is performed after initial completion, it is considered a servicing or workover operation.

If well tests indicate that the well is productive, then production tubing string(s) is run inside the production casing. The tubing string serves to carry well production to the surface. Testing procedures are conducted through the blowout preventers (BOP) and the tubing is also run with the BOP stack in place. The BOP stack is removed after temporary plugs are set in the tubing. Finally, the wellhead control assembly, termed a "Christmas tree," is connected to the tubing (U.S. Geological Survey 1976).

After the pipes, tanks, and processing facilities are installed, seawater is pumped down the production casing of the well to flush out any remaining drilling mud (Clark et al. 1978). Downhole completion procedures vary greatly depending on reservoir conditions. The simplest completion technique is to perforate the production casing opposite productive intervals with gun (bullet) or jet (shaped-charge) perforations.

Subsea completion operations differ from the above described normal surface completion operations only in that, upon completion, the wellhead control assembly (i.e., Christmas tree) is situated on the ocean floor (U.S. Geological Survey 1976).

Production

In their initial completion stage, most wells will flow naturally to the surface because their reservoir pressure is high enough to support the column of reservoir fluid in the production tubing and deliver it to the surface. If reservoir pressures are insufficient to lift oil to the surface, gas may be injected under pressure down the casing. Gas lift is not practical in all wells and is usually a temporary measure. It is practical only as long as reservoir pressure remains fairly high. Almost all wells, at some stage in their productive lives, require artificial lift to bring production to the surface. Either submersible (i.e., rotary type) or hydraulic (i.e., piston type) pumps are usually used in offshore applications. Both pumping methods require little surface space and can be used in platform operations. Some models of the hydraulic pump are particularly suitable for subsea applications (U.S. Geological Survey 1976).

Once a well is completed and connected to production facilities, production may begin. If oil, gas, and other materials are produced, they must be separated (Figure 9).

The oil is separated, metered, and pumped, either to shore by pipeline, to offshore storage tanks, or to a tanker. If water is produced with the oil, a "free water knock-out" tank is often used to remove water that is not contained in an oil-water emulsion. If water is produced as an emulsion with the oil or if the oil is mixed with sand, more sophisticated equipment is needed (Kash et al. 1973). Separated water may be discharged to the ocean; however, the maximum allowable oil content is 100 parts per million (ppm) and the average allowable oil content is 50 ppm or less. Sand may be discarded into the ocean after the oil has been removed (Council on Environmental Quality 1974).

The gas is separated, pressurized, metered, and pumped to shore by pipeline. If there is no gas pipeline or if gas production is not economical, the gas may be pressurized and reinjected into the reservoir. If water is produced with the gas, the gas is dehydrated by contact with glycol.

When treatment facilities are mounted on production platforms, the equipment is similar, if not identical, to onshore production facilities (Kash et al. 1973). For subsea production, the processes

FIGURE 9
TYPICAL PRODUCTION FACILITY

remain essentially the same, but the hardware becomes much more complex. The problems of extensive subsea operations may be so severe or expensive that it may be preferable to transport the produced materials (i.e., oil, gas, water, and sand) either to platforms or to onshore facilities for treatment (Kash et al. 1973).

Due to the potential for explosions, fire, storms, and earthquakes, many devices are installed to warn of impending or existing dangers and to control or stop the flow of oil and gas if trouble is sensed. Production platforms may be equipped with pressure, level, and combustible gas sensors; manual and automatic pressure relief valves; and fire detection and fighting equipment. All wells also are equipped with a subsurface safety valve which can shut down the well in case of surface equipment failure.

Production activities are continuous and hardware is installed for the life of the field (Kash et al. 1973). However, it may be necessary to shut down and reenter a well to improve or restore production. A variety of operations may be involved in workover and servicing, including further drilling to deepen the well.

Transportation

Oil and gas may be transported to onshore processing facilities either by pipeline or by bulk carriers such as tankers and barges. To date, natural gas has been transported only by pipeline. During the early stages of an oil field's development, small amounts of gas are sometimes vented or flared. All of the oil produced off the California coast and 98 percent of Gulf of Mexico oil is transported to shore by pipeline (Kash et al. 1973). Nevertheless, barges and tankers are used as a temporary means of transportation during field development or to transport oil from fields with low production rates. Tankers are also used for supplemental transportation after pipelines are completed.

Pipelines

Pipelines transport large volumes of oil and natural gas. Once a pipeline route is selected and the volume to be pumped is determined, pipe size and strength are selected and line pressures calculated. Factors considered during the route selection process include: ocean bottom and subsurface foundations; current, wave, and tide conditions; and other uses of the area (e.g., fishing, shipping).

There are three primary techniques used to lay pipeline offshore: stove pipe, reel barge, and pipe pulling (Kash et al. 1973). In the stove pipe method, short sections of pipe are welded together

on a pipelaying barge; then they are released into the water and laid on the ocean floor as the barge moves forward. There are several types of barges and several ways to lower the pipe. The vessel may have a barge or ship hull or it may be a semisubmersible. The barge hull is the most common, although its operation is limited to relatively calm seas. The main advantage to this method is that any diameter of pipeline can be laid, but laying proceeds at a relatively slow rate (Council on Environmental Quality 1974; U.S. Geological Survey 1976).

In the reel barge method, pipe is welded together onshore and is wound onto a large reel on the pipelaying barge. The pipe is laid as it unwinds. This technique is limited to pipe diameters of 12 inches or less (Council on Environmental Quality 1974). The pipe pulling method uses barges and tugs to pull sections of welded pipe from an onshore launchway over the pipeline route. This method is limited to use for distances of only 2 to 4 miles off shore (Kash et al. 1973).

Offshore pipelines may be buried for several reasons, the most important being to ensure that the line will not be damaged. Damage to pipelines may be caused by anchors, fishing operations, currents, and storm waves. A burial barge is used to sink the pipe beneath the surface, usually by displacing soil with a high-pressure water jet (Kash et al. 1973; U.S. Geological Survey 1976).

Tankers and Barges

Tankers and barges transport less than 3 percent of the oil produced in the Gulf of Mexico. However, in 1972 the Atlantic Coast states received 91 percent of their domestic crude oil supply by tanker and barge from the Gulf of Mexico, and 89 percent of their foreign crude oil imports by tanker and barge (Council on Environmental Quality 1974). Transportation by Very Large Crude Carriers (VLCC) or supertankers is economically advantageous only over great distances (e.g., from the Persian Gulf to the U.S.).

Oil pollution from tankers and barges can occur either during transfer operations or as a result of collisions and groundings (Kash et al. 1973). Another major source of oil pollution from tankers is intentional discharge--the pumping of oily ballast water and tank washings into the ocean (Figure 10).

Offshore Storage

Offshore storage facilities can provide a buffer between the continuous production of wells and the discontinuities of tanker operations (Kash et al. 1973). Bottom standing concrete gravity

(1) After discharging its cargo, stability considerations require the tanker to take on ballast water in some of its empty cargo tanks. En route, the oil and water separate, and oil floats on top of the clean water. Meanwhile, other cargo tanks are cleaned and their oily residues pumped to a holding tank. (2) The cleaned tanks are filled with sea water, the original ballast water, now separated from the oil, is pumped overboard, and the remaining oil and oily water go to the holding tank. (3) The oil and oily water are carried to the ship's destination, where the clean ballast water is pumped overboard, and the next cargo of crude is loaded on top of the retained residues.

FIGURE 10
LOAD ON TOP TECHNIQUE

platforms and floating storage tanks with capacities of up to 1 million barrels each are being used in the Persian Gulf and the North Sea. Offshore storage technology has been developed primarily in response to needs in other parts of the world. However, offshore storage will be necessary for subsea completion systems in very deep fields because of the economics of tanker transport versus pipelines (Ranney 1979).

Offshore Oil Ports--Complex Facilities*

Culminating over 6 years of planning, hearings, and preparation, the Louisiana Offshore Oil Port (LOOP; the first American deepwater port capable of unloading supertankers) is under final construction. This may be the forerunner of a trend toward the greater use of the continental shelf for complex oil and gas storage and handling facilities. Initially, LOOP's operation will have a 1.4 million bbl-per-day throughput capacity. About half of the crude will be transported to Louisiana refineries and the other half will be piped to refineries in the Midwest.

Offshore Facility

The LOOP Marine Terminal is located approximately 19 miles offshore, and will be operated as a common carrier system. The entire LOOP system includes 19 miles of offshore pipeline and 28 miles of pipeline through the marshland between the shoreline and the Clovelly Salt Dome, where crude oil will be temporarily stored. The LOCAP pipeline (pipeline connecting the LOOP to the Capline pipeline) will be constructed across 53 miles of marsh, swamp, forest, and agricultural land between the Clovelly Salt Dome and the St. James, Louisiana, terminal, where the Capline pipeline will carry the oil to the Midwest.

Arriving tankers of up to 700,000 dead weight tons (dwt) will be guided by a specially trained mooring master to one of three single-point mooring buoys, where they will be able to rotate 360 degrees around the buoy. This will enable the ship to maintain a heading of least resistance to wind and waves during offloading operations. The port is located in 110 feet of water in Grand Isle Block 59 in the Gulf of Mexico off the coastline of Louisiana.

All pipe entering and leaving the platform has a minimum of 10 feet of cover along a 500-foot section of line adjacent to the platform. The rest of the line has a minimum cover of 3 feet until the

*Information in this section is taken largely from Dietsch 1980.

shoreline approach, where the line is buried to provide a minimum depth of 10 feet below mean low water.

Onshore Facilities

Connecting the platform with the onshore facilities is a 48-inch underwater pipeline that carries the oil to the Fourchon Booster Station on the shore. Oil will then move through a 48-inch line to the Clovelly Salt Dome Storage Terminal containing eight subsurface cavities, each with a storage capacity of 4 million barrels. The individual cavity system is essential because LOOP will be handling six different segregations of foreign crude. The crude is pumped into these storage cavities by 6,000-horsepower electrically powered pumps. These eight cavities have a total capacity of 40 million bbls. There will also be a 25 million-bbl brine storage reservoir, fire protection facilities, crude oil pumps, and power and communication facilities. In addition, the terminal provides space for originating pump stations for six future outgoing pipelines. This 48-inch line is about 29 miles long. Another 29 miles of 30-inch brine line from the Clovelly Storage Facility extends 2 miles into the Gulf.

System Supervisory Control

The LOOP supervisory control and monitoring system is comprised of an integrated array of digital computers, peripheral devices, communications links, and programmable controllers. The system is designed to allow operational control and full monitoring of the entire LOOP facilities from the Operations Center at Galliano. The interface to the pipeline will be via the programmable controllers, which also function as the primary process control system. Local digital processors and associated man-machine interfaces will be located at three major facilities: the Marine Terminal, Fourchon Booster Station, and Clovelly Dome Storage Complex.

Future LOOP Phases

Possible future LOOP plans include phase II, when throughput would reach 2.4 million bbls per day with the addition of one single point mooring unit and connecting 56-inch line, one 48-inch line to shore, one 48-inch line to Clovelly, 10 million bbls of additional storage capacity, and added pumping capacity at all pump stations.

Other Deep Water Ports

Recently the U.S. Army Corps of Engineers issued a dredging permit to the Port of Galveston and Pelican Terminal Corporation to proceed with construction and use of the deep channel and pipeline

system to support the Gulf Coast's first onshore deep-draft oil terminal. The Pelco (Northville Industries-Chicago Bridge & Iron joint venture) crude oil terminal will be located on Pelican Island, sheltered from the Gulf of Mexico by the island of Galveston, and have two tanker unloading berths capable of serving ships up to 250,000 dwt, lightened to a draft of 50 ft. Oil unloaded at the facility will be shipped by twin pipelines to a storage farm on the mainland at Texas City, from which delivery pipelines will fan out to refineries near Houston, Port Arthur/Beaumont, and possibly Freeport, Texas. Construction is slated to begin in early 1981 and port operation is expected to begin in late 1982 (Pipeline and Gas Journal 1980).

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HEALTH EFFECTS OF OFFSHORE DEVELOPMENT

Offshore oil and gas production would have its greatest potential impact on human health within the workplace, although the general public could be affected if the industry causes contamination of the marine food chain leading to man and the emission of airborne pollutants from offshore production or port complexes. Federal agencies concerned with health and safety on offshore oil platforms include the Environmental Protection Agency, U.S. Geological Survey, Department of Energy, National Marine Fisheries Service, Food and Drug Administration, U.S. Coast Guard, Occupational Safety and Health Administration, and the National Institute for Occupational Safety and Health.

This section presents an overview of potential health and safety problems related particularly to offshore oil and gas production and it provides directions for future research. The reader is referred to the Onshore section for discussions of health problems generally associated with exploration for and extraction of oil and gas.

Occupational Health Considerations

Individuals involved in offshore oil and gas development operations may be subjected to potentially hazardous chemicals. It is expected that dermal exposure to drilling muds and associated chemicals, and pulmonary exposure to air pollutants and flare gases are frequent.

Drilling Muds

Drilling mud is a chemically complex mixture of clay, water, and numerous chemical additives. Chemical ingredients used to formulate various muds can include pH-control products, bactericides, calcium-removers, corrosion inhibitors, defoamers, emulsifiers, filtrate reducers, flocculants, foaming agents, lost circulation materials, lubricants, shale-control inhibitors, surface-active agents, thinners, dispersants, viscosifiers, and weighting agents (Richards 1979). The frequency of dermal exposure to these substances for offshore oil rig workers is not known and the effects of these substances on occupational health has not been thoroughly explored. On offshore platforms, drilling muds are known to discolor the skin of workers and to present a safety hazard when it coats surfaces, making them slippery. Additional information on the health effects associated with drilling fluids is contained in the Onshore section of this report under Health Effects. Research is needed to determine the extent and severity of adverse effects from exposure to these substances. For those found to represent hazards, methods should be developed to limit occupational exposure.

Hydrogen Sulfide

A severe occupational health hazard on offshore drilling platforms is exposure to hydrogen sulfide. A few breaths of highly concentrated hydrogen sulfide escaping from the drill hole can result in paralysis of the diaphragm, causing a cessation in breathing. On most platforms, sensors designed to detect hydrogen sulfide in high concentrations trigger a wailing siren to alert workers to move upwind, use walk-around air cylinders, or possibly, to embark on escape capsules. So deadly is the gas that prospective workers with poor hearing may not be allowed on the platform.

The hydrogen sulfide hazard may be compounded by another hazard--the impaired hearing of workers exposed to a high noise level on offshore drilling platforms. The noise is associated with the continuous use of diesel engines, metal striking metal, operation of cable and drum, and use of winches and chains. Communication by word of mouth is difficult and workers usually watch each other's hands and eyes to avoid injury.

Health Statistics

Occupational injuries and illnesses for 1978 for various stages of oil and gas development are listed in Table 1. This information was obtained by the American Petroleum Institute from 109 oil and gas companies employing over 435,000 persons with a total work experience of more than 890 million hours. The incidence rate (i.e., total recordable cases per 100 full time workers) was found to be 4.47 for 1978, compared with 4.52 for 1977 (American Petroleum Institute 1979a). Occupational accident data are summarized on an energy equivalent basis in Table 2 and in terms of supplying a 1,000-megawatt power plant with fuel for 1 year in Table 3.

Occupational Safety Considerations

Accidents involved in the development of offshore oil and gas reserves can occur at any stage of development. These accidents can involve equipment failure, human error, and natural phenomena. The consequences can include occupational injury or death. Workers may be injured by falling objects, swinging sections of pipe or block and tackle, uncontrolled torques in the drill stack, coupling pipe sections, blowouts, oil platform fires, oil spills or pipeline leaks, and by transportation vehicles (e.g., helicopters).

For comparison purposes, a breakdown of fatalities for 1977 and 1978 is presented in Table 4 for 109 oil and gas companies employing 435,524 workers. There were only 75 on-duty fatal accidents during 1978. This is equivalent to one fatality for every 5,807 workers

TABLE 1

REPORT OF OCCUPATIONAL INJURIES AND ILLNESSES FOR 1978^a

1	2	3	4	5			6						7		
Function	SIC	Number of Employees	Hours Worked (Thousands)	Recordable Cases			Extent and Outcome of Injuries and Illnesses						Incident Rates		
				a.	b.	c.	d.	e.	f.	g.	h.	i.	j.	k.	l.
				Injuries	Illnesses	Total	Fatalities	Lost Workday Cases				Non-Fatal Cases Without Lost Workdays	Total Cases	Fatalities Plus Cases With Days Away From Work	Lost Workday—Days Away From Work
								Total Cases	Cases Involving Days Away From Work	Number of Days Away From Work	Number of Days of Restricted Activity				
Exploration & Production	1311	72,749	148,508	2,758	51	2,809	21	1,157	1,076	20,045	1,923	1,631	3.78	1.48	27.00
Gas Processing	1321	7,220	14,758	318	7	325	3	100	98	1,756	240	222	4.40	1.37	23.80
Drilling	1381	2,947	6,692	809	1	810	1	331	317	9,337	117	478	24.21	9.50	279.05
Chemicals	2800	42,909	97,656	2,944	116	3,060	3	1,130	729	16,034	6,092	1,927	6.27	1.50	32.84
Refining	2911	81,168	165,244	4,688	294	4,982	19	2,386	1,116	27,555	12,995	2,597	6.03	1.37	33.35
Marketing-Wholesale	5171	53,747	112,224	2,743	8	2,751	10	1,559	1,442	23,230	1,724	1,182	4.90	2.59	41.40
Marketing-Retail	5541	36,982	68,443	1,519	12	1,531	7	776	624	9,140	1,464	748	4.47	1.84	26.71
Pipeline-Crude and Products	4610	13,536	27,010	601	21	622	1	165	154	2,649	141	456	4.61	1.15	19.61
Pipeline-Gas	4922	18,551	35,854	859	15	874	1	180	173	3,245	918	693	4.88	.97	18.10
Marine	4400	3,906	16,242	284	10	274	2	134	130	4,259	55	138	3.37	1.63	52.44
Research and Development		17,237	33,258	315	15	330	1	106	73	584	844	223	1.98	.45	3.51
Engineering & Gen. Service		8,255	15,528	195	5	200	0	49	41	595	247	151	2.58	.53	7.66
Miscellaneous		61,923	121,048	687	16	703	4	347	286	3,245	487	352	1.16	.48	5.36
Combined Functions		14,394	28,148	623	7	630	2	322	248	4,948	828	306	4.48	1.78	35.16
Total		435,524	890,613	19,323	578	19,901	75	8,722	6,507	126,622	28,075	11,104	4.47	1.48	28.43

Incidence rates (column 7) are calculated as follows:

$$\text{Column 7(j)} = \frac{\text{Column 5(c)} \times 200,000}{\text{Column 4} \times 1,000}$$

$$\text{Column 7(k)} = \frac{\text{Column 6(d)} + 6(f) \times 200,000}{\text{Column 4} \times 1,000}$$

$$\text{Column 7(l)} = \frac{\text{Column 6(g)} \times 200,000}{\text{Column 4} \times 1,000}$$

^aCovers operations subject to OSHA recordkeeping requirements only.

Source: American Petroleum Institute 1979a

TABLE 2
OCCUPATIONAL ACCIDENTS FOR CRUDE OIL
AND PRODUCT TRANSPORT AND REFINING

System	Accident Rate per 10^{12} Btu Equivalents		
	Fatalities	Injuries	Man-Days Lost
Crude Oil			
Pipeline	6.9×10^{-5}	4.2×10^{-3}	1.0
Pipeline	0.009	0.008	15.0
Oil tanker	0.0009	0.008	15.0
Oil barge	0.0009	0.008	15.0
Product distribution pipeline	6.9×10^{-5}	4.2×10^{-3}	1.0
Canadian crude/imported			
Uncontrolled	4.4×10^{-4}	0.0362	2.05
Controlled	4.4×10^{-4}	0.0362	2.05
Middle East crude/imported			
Uncontrolled	4.4×10^{-4}	0.0362	2.05
Controlled	4.4×10^{-4}	0.0362	2.05
Conventional refinery			
Arabian crude	0.0014	0.11	25.0
Kuwait crude	0.0014	0.11	25.0

Source: University of Oklahoma 1975.

TABLE 3
ANNUAL DEATHS, INJURIES, AND WORKDAYS LOST FOR
UNCONTROLLED OIL-FIRED ELECTRICITY SYSTEMS

	Extraction		Processing	Transport			Conversion	Total		
	Onshore	Offshore		Onshore	Offshore	Import		Onshore	Offshore	Import
Deaths	0.21	0.21	0.08	0.05	0.05	0.5	0.010	0.35	0.35	0.06
Injuries	21	21	5.6	4.5	4.5	4.5	1.15	32.3	32.3	5.7
Workdays lost	2,135	2,135	785	562	562	562	127.2	3,609	3,609	689

Source: Council on Environmental Quality 1973.

TABLE 4
FATALITIES BY FUNCTIONS AND CAUSES

Function	<u>Cases Reported</u>		<u>Fire and Explosion</u>		<u>Struck by Equipment</u>		<u>Motor Vehicle</u>		<u>Aircraft</u>		<u>Other Causes</u>	
	1978	1977	1978	1977	1978	1977	1978	1977	1978	1977	1978	1977
Exploration and production	19	23	1	2	2	3	0	2	7	15	9	1
Gas processing	0	1	0	0	0	0	0	1	0	0	0	0
Drilling	0	0	0	0	0	0	0	0	0	0	0	0
Chemicals	1	0	0	0	0	0	0	0	0	0	1	0
Refining	5	11	4	9	0	0	0	0	0	0	1	2
Marketing												
Wholesale	8	15	1	5	1	0	5	9	0	0	1	1
Retail	2	4	0	0	0	0	0	1	0	0	2	3
Pipeline												
Crude and products	0	1	0	1	0	0	0	0	0	0	0	0
Gas	1	0	0	0	0	0	0	0	0	0	1	0
Marine	2	1	0	0	0	0	0	0	0	0	2	1
Research and development	1	0	1	0	0	0	0	0	0	0	0	0
Engineering and general services	0	0	0	0	0	0	0	0	0	0	0	0
Miscellaneous	4	0	0	0	0	0	0	0	0	0	4	0
Total	43	56	7	17	3	3	5	13	7	15	21	8

Source: American Petroleum Institute 1979b.

employed--a slight increase over 5,995 in 1977 (American Petroleum Institute 1979b).

Drilling Rig Accidents

Recently the popular press and some trade journals reported on serious accidents associated with offshore drilling (Downie 1980; The Washington Post 1980; U.S. News and World Report 1980; Mathews 1980). The reported incidents exposed the dangers of offshore drilling and attracted the attention of the public and regulatory agencies to the industry's safety hazards.

In a North Sea accident March 27, 1980, the oil rig Alexander L. Kielland collapsed and 123 lives were lost (Downie 1980). This semi-submersible rig with pontoon legs was considered to be almost incapable of capsizing. Consequently, most safety precautions against a large-scale disaster were designed for blowouts. Water safety precautions apparently did not anticipate a rig collapsing so quickly (Downie 1980). The builder and the owner of the rig are not sure what caused the accident and investigations are underway. Theories range from simple metal fatigue not discovered in routine inspections, to the snapping in a stormy sea of one of the anchor cables that secured the submerged pontoon legs to the ocean floor. The current and most likely theory is that a leg collapsed due to a crack originating from a hole created to hold a sensing device. Whatever the reason, the number killed in this single accident exceeded the 102 who have died in all deep-water oil exploration in the British sector of the North Sea since the mid-1960s (Downie 1980).

A gas drilling rig explosion about 100 miles southeast of Galveston took place just 3 days before the North Sea tragedy. Twenty-nine persons were injured and six were killed in this accident. Another rig explosion occurred recently about 110 miles south-southeast of Intercoastal City where a Marathon Oil Company drilling platform exploded and caught fire (The Washington Post 1980). There were no fatalities, but several persons were injured. Although human error is blamed for most of these recent accidents, causal factors are still being investigated.

In July 1980 an offshore Chinese mobile oil rig exploded and collapsed in the Bohai Gulf off China's east coast, killing 72 workers. The accident was attributed to failure to follow safety rules during movement of the rig in high winds. In addition, 1,043 other offshore accidents near China from 1975 to 1979 resulted in 105 deaths and 114 serious injuries (Mathews 1980).

U.S. offshore incidents have increased in recent years. In 1978, 1,144 wells were started in domestic waters and 58 incidents

were reported. In contrast, 900 wells were started in 1970 and only 24 incidents were reported (Gillan 1980a). In spite of the recent increase, little is being done to collect data on offshore drilling rig accidents. Seeking information, MITRE contacted a number of private organizations--the American Petroleum Institute (API), International Association of Drilling Contractors (IADC), AFL-CIO, and the Offshore Rig Data Service--as well as government agencies, including the Occupational Safety and Health Administration (OSHA), Bureau of Labor Statistics (BLS), and the U.S. Coast Guard. Most of the private organizations do not segregate their data by drilling site, although the Coast Guard is making efforts in this direction. Offshore Rig Data Service and IADC are the only organizations contacted that have some information in this area. Considering its data to be confidential, the latter makes its information available only to regulatory agencies or its own members. The former did supply some information which is summarized in the following section.

Summary of Offshore Accidents

In an attempt to comprehend the nature, type, and severity of accidents associated with offshore drilling rigs, a review of available data and information from various sources was conducted.

The data supplied by Offshore Rig Data Service (1980) covers 1955 to early 1980 and primarily concerns mobile rigs; few data relate to fixed platforms. Five major types of accidents (based on their causes) are discernible from this data:*

- o Blowouts/fires;
- o Structural/equipment failure;
- o Natural disaster damage (storms, hurricanes);
- o Capsizings; and
- o Miscellaneous (collisions, sinkings).

All types of accidents (except for blowouts) can occur in either of two operations: drilling or towing. However, capsizings and collisions seem to be more frequent during towing (capsizings also occur during preparations for towing) and most fires occur during drilling while the rig is still active. Generally, due to the necessity for frequent set-up, unfamiliarity with the rig, and lack of ideal stability, mobile rigs are more susceptible to accidents than fixed platforms. During the drilling operation, the most disastrous

*This categorization is arbitrary and is designed to organize the available information. It should not, therefore, be considered a standardized classification.

situation is a blowout, which can affect the rig and its occupants in several ways. Should the gas or product ignite after a blowout, the drilling rig could easily catch fire, resulting in total destruction. A blowout around a subsea wellhead could create sufficient aeration of the water to alter water density, causing the vessel to sink. An effect on jack-ups, or any rig permanently anchored to the bottom, would be scouring around mats, legs, or other bottom supports due to escaping gas, which could cause foundation failure and subsequent rig damage. Table 5 shows the occurrence of these five types of accidents from 1955 to February 1980.

Over the 25-year period, 173 accidents were reported. The greatest percentage (38 percent) were attributable to natural disasters. About 27 percent resulted from blowouts or fires, and 22 percent from structural or equipment failure. Twelve injuries and 116 fatalities were reported during this period.

The data also reveal that accidents related to offshore mobile rigs have been steadily increasing since 1970. To a large extent this trend reflects an increase in activity by old and newly commissioned drilling rigs. Between 1949 and 1976 the offshore fleet grew from 1 to 345 operating rigs (Huff 1976). In September 1979 it had expanded to 512 vessels--30 submersibles, 88 drillships and barges, 123 semisubmersibles and 271 jack-ups (Tubb 1979). By September 1980 this fleet has grown to 606 units (Trafford 1980).

Extrapolation of industry-wide accident rates from this information should be attempted with extreme caution because these data are for mobile rigs only. By nature of their activity, they are involved in accidents while moving off location or preparing to move.

The offshore fixed platform drilling industry can be a dangerous business, as indicated by a recent study that reported a high rate of fatalities for young men working on oil rigs in Louisiana. The study identified 205 occupational deaths among oil workers within a 6-year period (January 1973 to December 1978). Of those who died, about 1/3 were on land-based platforms, all were males, and a majority (about 57 percent) were under 30 years old. Around 66 percent of the deaths occurred on offshore platforms and 69 percent of the accidents took place during daylight hours. They occurred throughout the year with no seasonal or monthly predominance (Morbidity and Mortality Weekly Report 1980).

Trauma and drowning accounted for a majority of deaths (80 percent); 1/4th were attributable to workers being struck by heavy objects; and about 21 percent resulted from tragic events such as explosions, fires, or helicopter crashes (Morbidity and Mortality Weekly Report 1980).

TABLE 5
OFFSHORE RIG ACCIDENTS

Year	Blowouts/ Fires	Structural/ Equipment Failure	Damage from Natural Disasters	Capsizings	Miscellaneous (collisions, sinkings)	Total
1955	1		1	1		3
1956						0
1957			2	2	1	5
1958			1	1		2
1959	1			1		2
1960			1			1
1961			3		1	4
1962			1			1
1963						0
1964	1		1			2
1965	2		1	1	4	8
1966		1	1	1		3
1967						0
1968	2		6	1		9
1969	3		9	1		13
1970	5	3	6		1	15
1971	3		2			5
1972	4	1	2			7
1973	1	2	3			6
1974	3	9	7	1		20
1975	4	3	3	1	1	12
1976	3	2	9	1		15
1977	2	5	3	1		11
1978	3	5				8
1979	6	3	2	1	2	14
1980 (Feb.)	2	4	1			7
Total	46	38	65	14	10	173

Source: Offshore Rig Data Service 1980.

It is estimated that 25 percent of workers engaged in oil and gas production in Louisiana in 1978 worked full time on active oil rigs. The mortality rate for this group is estimated to be 188 to 235 per 100,000 workers per year. This compares to a mortality rate of 14 in 100,000 for all U.S. workers and 57 in 100,000 for those in construction, a relatively high risk industry (Morbidity and Mortality Weekly Report 1980).

Offshore Safety Problems

In the case of the North Sea accident involving the Alexander L. Kielland, the oil companies spent millions of dollars installing safety precautions on the offshore rigs. Moreover, instructing workers in safety was a company priority (Boyne 1980). The Coast Guard, IADC, and the drilling industry attribute such accidents to human error. Most can be traced to people problems: lack of training, negligence, or a lapse in safety practices, even among workers who know better (Gillan 1980b). A preliminary analysis of the Louisiana accidents indicated that factors contributing to a high rate of rig accidents include rapid turnover of personnel, lack of formal work training programs, and problems with regard to regulation of the industry (Morbidity and Mortality Weekly Report 1980). Shell Oil Company statistics show that people problems were responsible for 75 percent of all lost-time accidents during offshore drilling and production. The other 25 percent resulted from a combination of personnel and equipment failures. Even the causes of collapses are seldom beyond human control (Gillan 1980a).

Personnel turnover resulting from constant mobility of the rigs has been cited as one problem affecting personnel training. The accident rate is assumed to be higher with new employees. No hard data are available to substantiate this assumption, but records kept by the Ocean Drilling and Exploration Company indicate that 68 percent of all lost-time injuries were sustained by workers in their first 12 months of offshore duty (Gillan 1980a).

Illegal drug use by offshore workers is also considered to be responsible for accidents. Many petroleum and drilling companies have instituted anti-drug courses, conducted unannounced searches, and stationed "sniffer" dogs on offshore rigs and platforms to seek out marijuana. After an anti-drug program was begun, some companies have reported 50 percent declines in their accident rates, less employee turnover, and fewer losses from thefts. Use of alcohol is also believed to contribute to accidents (The Washington Post Magazine 1980).

Another factor contributing to poor safety records aboard drilling platforms is low morale. Freedom from boredom and good food can

be expected to raise morale, while poor food, poor television reception and programming, and a lack of rapport with management could lower morale (The Washington Post Magazine 1980).

Irrespective of the human error factor and personnel training problems, both the Coast Guard and the International Association of Drilling Contractors have conceded that some drilling contractors have a poor safety record; however, because of high demand, they stay in business. The nation's energy crisis has forced operators to use drilling contractors they might ordinarily not use (Gillan 1980b). Drilling contractors are believed to have higher accident rates than company-owned rigs, but at present there is no way to check a contractor's safety record. Information can only be obtained from the firm or by listening to rumors in the petroleum industry. Neither of these sources can offer dependable guidance in selecting the most crucial safety factor in offshore drilling--the drilling contractor.

Safety problems may be aggravated as countries with scant oil exploration experience, such as those in Latin America and Africa, enter into the offshore drilling business. Experts caution that the underwater quest for petroleum may be accompanied by greater disasters before this decade is over (U.S. News and World Report 1980).

A change in the exploration environment has also been cited as a cause of offshore drilling accidents. Exploration now takes place far from shore--a practice unheard of a few years ago. The North Sea disaster, for example, occurred 175 miles off the coast of Norway. Locating a rig that far from the coast makes rescue operations more difficult and places the rig in a harsher environment. Mobile rigs have drilled wells in water as deep as 4,876 feet (Smith 1979) and one fixed platform operates in 1,025 feet of water in the Gulf of Mexico (Ocean Industry 1980).

An emerging field of study relating to offshore safety is human factors engineering. This field concentrates on creating a workplace environment that is compatible with the entire spectrum of the workforce. The University of Oklahoma is examining the role of human factors engineering in drilling rig safety.

Tanker Accidents*

Tanker accidents may result not only in oil spills, but also in injuries, deaths, and property losses. Table 6 summarizes data

*In-depth coverage of transportation problems is provided in the Transportation and Storage section.

TABLE 6

DEATHS AND INJURIES RESULTING
FROM TANKSHIP ACCIDENTS

Accident Type	Number	Deaths	Injuries
Breakdown	4	5	53
Collision	26	259	130
Explosion	33	46	47
Fire	14	34	10
Grounding	0	0	0
Ramming	0	0	0
Structural failure	6	37	32
Other	<u>0</u>	<u>0</u>	<u>0</u>
Total	83	381	178

Notes: For accidents involving vessels over 3,000 dwt. Deaths and injuries include those occurring on other vessels or ashore as a result of the accident.

These data are from an analysis by the U.S. Coast Guard's Office of Merchant Marine Safety. They cover 3,715 worldwide tankship accidents from 1969 through 1973.

Source: Card et al. 1975.

relating deaths and injuries to various types of accidents for 1971 to 1973. Most of the deaths and injuries were attributable to collisions and explosions (Card et al. 1975). The 381 deaths over a 3-year period is not a large number compared to 1,500 persons killed in the U.S. each year in recreational boating accidents.

Data are presented in Table 7 which indicate the extent of damage to ships involved (Card et al. 1975). Of the 3,183 accidents, 73 percent caused only minor damage, while 15 percent resulted in no damage. Only 1.6 percent of the accidents resulted in total loss. The actual dollar amount of the damage or losses depends on repair or replacement costs, lost business revenues, increased insurance premiums, and other factors for which no data were available.

Accident and damage descriptions for 47 of the 51 total losses are shown in Table 8. More than 1/3rd of the total losses were caused by structural failure and accounted for 44 percent of the oil outflow. Causes for the loss of structural integrity in the accidents are shown in Table 9 (Card et al. 1975).

Pipeline Accidents*

The occupational health hazards associated with pipeline accidents include fire and explosion with resulting injury and loss of life. Offshore oil and gas platforms are often connected to shore by pipelines. These pipelines cross coastal wetlands and uplands to connect with major transportation networks.

Liquid pipeline accidents caused approximately \$3.2 million in property damage, the loss of 7 lives, 15 injuries, and the loss of over 319,000 barrels of commodities during 1975 (offshore and onshore data are commingled). A summary of pipeline accidents for 1975 is shown in Table 10. A breakdown of accidents in terms of the commodity involved is shown in Table 11. It should be noted that, of the commodities lost as a result of accidents, crude oil represented 45.1 percent; gasoline, 28.3 percent; and liquified petroleum (LPG),

*In-depth coverage of oil and gas transportation is provided in the Transportation and Storage section.

TABLE 7

EXTENT OF TANKSHIP LOSS OR DAMAGE
(1969-1973)

Type of Involvement	Total Loss	Heavy Damage	Light Damage	No Damage	Damage Unknown
Breakdown	2	16	197	131	9
Collision	7	64	570	78	25
Explosion	11	30	52	10	1
Fire	1	26	149	14	7
Grounding	12	63	487	206	22
Ramming	0	23	412	35	3
Structural failure	15	39	445	2	14
Other	<u>3</u>	<u>1</u>	<u>1</u>	<u>0</u>	<u>0</u>
Total	51	262	2,313	476	81

Source: Card et al. 1975.

TABLE 8
ACCIDENT SEQUENCE FOR 47 TANKSHIP LOSSES^a
(1969-1973)

Accident Sequence	Number	Oil Outflow (long tons)	Oil Outflow (bbls)
Breakdown--structural failure--sink	1	16,350	123,933
Breakdown--grounding-- sink	1	13,000	98,540
Collision--sink	2	4,138	31,365
Collision--explosion/ fire--sink	4	136,163	1,032,116
Explosion/fire--sink	12	90,030	682,427
Grounding--explosion/ fire--sink	1	2,500	18,950
Grounding--sink	9	134,726	1,021,223
Flooding--sink	2	54,669	414,391
Structural failure-- grounding--sink	1	40,000	303,200
Structural failure-- sink	14	282,519	2,141,494
Total	47	774,095	5,867,640

Note: Conversion factor--long tons x 7.85 = bbls.

^aFor tankships over 10,000 deadweight tons.

Source: Card et al. 1975.

TABLE 9

DESCRIPTION OF LOSS OF STRUCTURAL INTEGRITY
FOR 47 TANKSHIP LOSSES^a (1969-1973)

Description	Number	Oil Outflow (Long Tons)
Loss of structural integrity of hull caused primarily by external forces or where local material conditions deteriorated. No explosion or fire was associated with the accident.		
Structural failure of main hull girder from excess bending or shear loading	12	243,619
Local structural failure of hull envelope		
Failure of hull penetration	2	36,750
Local hull plating failure	2	39,169
Unknown local structural failure	1	34,000
Hull damage caused by collision or grounding		
Collision	2	4,138
Grounding	11	187,726
Subtotal	30	545,402
Loss of structural integrity from damage caused primarily by explosion or fire or where explosion or fire con- tributed to loss of struc- tural integrity.		
Explosion or fire initiated in own ship cargo tanks	12	90,030
Explosion or fire set off by vessel collision or grounding		
Collision	4	136,163
Grounding	1	2,500
Subtotal	17	228,693

^aIncludes tankships over 10,000 deadweight tons.

Source: Card et al. 1975.

TABLE 10
LIQUID PIPELINE ACCIDENT SUMMARY^a

Cause of Accident	Number of Accidents	Percent of Total	Deaths		Injuries	
			Carrier Employees	Non-Employees	Carrier Employees	Non-Employees
Equipment rupturing line	75	28.6	0	0	0	1
Corrosion--external	57	22.4	0	0	0	0
Equipment failure	27	10.6	3	0	3	0
Incorrect operation by carrier personnel	22	8.6	0	0	0	0
Corrosion--internal	16	5.9	0	0	0	0
Defective pipe seam	19	5.9	0	0	0	0
Defective girth weld	5	2.0	0	0	0	0
Failure of previously damaged pipe	4	1.6	0	4	0	9
Vandalism	4	1.6	0	0	0	0
Failure of previous weld repair	2	0.7	0	0	0	0
Lightning	2	0.7	0	0	0	0
Miscellaneous	<u>29</u>	<u>11.4</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>2</u>
Total	262	100.0	3	4	3	12

^aFor January 1, 1975 through December 31, 1975.

Source: U.S. Environmental Protection Agency 1977.

TABLE 11
PIPELINE ACCIDENT SUMMARY BY COMMODITY INVOLVED

Commodity	Number of Accidents	Percent of Total	Loss in Barrels	Percent of Total	Property Damage (\$)			Percent of Total	Deaths		Injuries	
					Carrier	Other	Total		Carrier Employees	Non- Employees	Carrier Employees	Non- Employees
Crude oil	135	52.9	105,871	33.14	1,293,923	147,841	1,441,764	45.1	1	0	0	1
Gasoline	41	16.1	30,843	9.7	771,223	134,281	905,504	28.3	0	0	0	1
Fuel oil	29	11.4	24,386	7.63	38,401	14,000	52,401	1.6	0	0	0	0
LPG	26	10.2	105,228	32.94	269,870	416,000	685,870	21.5	2	4	3	10
Jet fuel	7	2.7	4,249	1.33	462	5,000	5,462	0.2	0	0	0	0
Natural gasoline	7	2.7	21,475	6.73	916	94,210	95,126	2.96	0	0	0	0
Kerosene	4	1.6	25,030	7.84	6,919	2,150	9,069	0.28	0	0	0	0
Anhydrous ammonia	3	1.2	1,311	0.41	10	1,000	1,010	0.03	0	0	0	0
Condensate	2	0.8	850	0.27	475	100	575	0.02	0	0	0	0
Transmix	1	0.4	180	0.01	0	300	300	0.01	0	0	0	0
Total	255	100.0	319,423	100	2,382,199	814,882	3,197,081	100	3	4	3	12

Source: U.S. Environmental Protection Agency 1977.

21.5 percent. Accidents involving LPG accounted for 86 percent of the deaths and 87 percent of the injuries.*

Approximately 43 percent of the 78 accidents caused by equipment rupturing were the result of bulldozer, grader, and ditching machine operation. Of these 78 accidents, 47 percent involved the following activities:

- o Pipeline and cable construction (12 accidents, 16.4 percent);
- o Moving earth by commercial firms or local government (11 accidents, 15.1 percent); and
- o Clearing or grading private land (11 accidents, 15.1 percent).

Although the bulk of these accidents relate to land-based oil and gas transportation, hazards relating to these causes of accidents also exist for offshore pipelines crossing shallow bogs, coastal wetlands, and coastal upland areas. Often, longshore flatlands serve as transportation corridors, with railroads, gas and oil pipelines, water and sewage lines, electric lines, and buried telephone lines.

*Injury and fatality statistics are always subject to discrepancies due to non-uniform or incomplete reporting. Statistics quoted in this section come from the U.S. Department of Transportation (DOT) and are based on DOT 7000-1 forms filed during 1975. The American Petroleum Institute (API) also has published data for 1975 based on information collected from 137 oil and gas companies and their subsidiaries. The API data are for the entire industry and are further divided by function (e.g., exploration and production, drilling, pipeline-crude, and products). Comparison of the appropriate API and DOT data for pipeline (crude and liquid) shows significant differences between the two sets of data:

	<u>API</u>	<u>DOT</u>
Injuries (lost-time)	754	15 employee and non-employee
Fatalities	6	7 employee and non-employee

The API fatalities include tank truck accidents while the DOT figures apparently do not.

The potential exists for compounding the dangers inherent in each of these transportation systems.

The DOT statistics also showed that 78 percent (57) of the corrosion-caused accidents were due to external corrosion. This would be expected to occur with old pipelines since newer ones generally have protective coatings and cathodic protection. Seventy-two percent were in equipment installed between 1920 and 1949 (Table 12). However, 75.5 percent involved lines with cathodic protection. External corrosion accidents accounted for approximately \$115,800 in property damage, but resulted in no deaths or injuries. Two-thirds of external corrosion accidents involved crude oil in the pipeline, while the remainder involved gasoline (15.8 percent); fuel oil (12.3 percent); and jet fuel, furnace oil, and transmix (5.3 percent).

Pipeline spills were the second largest source of oil pollution in coastal waters (Boesch et al. 1974). In 1971, 1,436 leaks spilled 897,685 gallons. An evaluation of spill data indicates approximately 90 percent of offshore spills and 97 percent of all oil spilled comes from pipelines leading to wells less than three miles offshore. Most of the pipeline spillage results from the failure of old pipelines.

Pipeline accidents are caused by a number of factors, including equipment rupturing lines, internal and external corrosion, structural defects (seams, welds, repairs), human operating errors, vandalism, and natural causes. According to the U.S. Department of Transportation's Office of Pipeline Safety Operations, equipment rupturing lines (28.6 percent) and external corrosion (22.4 percent) accounted for about half of the accidents during 1975 (U.S. Department of Transportation 1976). These accidents caused an estimated \$757,500 in property damage and a loss of 120,797 barrels of oil, or 38 percent of the total oil lost in pipeline accidents.

Public Health and Safety Considerations

This section considers public health and safety issues which may result from the development of offshore oil and gas reserves. Under most circumstances, it can be assumed that any adverse human health effects associated with development drilling, well completion, and production operations were experienced primarily by workers involved with these operations. However, the potential does exist for the general public to be adversely affected by these operations. The location of offshore oil and gas activities, their proximity to urban areas, and local atmospheric transport processes must be considered.

Atmospheric emissions associated with offshore transportation operations may be considerable, although it is believed that the impact can be greatly reduced with proper controls on tankers and

TABLE 12
PIPELINE ACCIDENTS

Property Damage (in dollars)			Loss of Commodity (bbls)	Number of Accidents by Year of Installation							Year Not Reported
Carrier	Other	Total		Before 1920	1920- 1929	1930- 1939	1940- 1949	1950- 1959	1960- 1969	1970- 1975	
375,110	266,751	641,681	83,724	3	9	3	19	14	21	3	1
89,931	25,850	115,781	37,073	2	10	17	14	9	3	1	1
543,010	9,081	543,091	20,981	0	0	2	1	2	10	8	4
654,705	128,150	782,855	26,619	0	1	3	3	1	8	5	1
2,890	2,550	5,440	2,853	0	6	0	2	2	6	0	0
2,259	12,650	14,909	61,570	0	2	3	4	2	7	1	0
4,150	2,015	6,165	30,131	0	0	3	0	1	1	0	0
20,260	363,000	383,260	31,665	0	0	1	0	1	1	1	0
3,505	15	3,520	884	0	0	1	2	0	1	0	0
17,450	1,500	18,950	2,739	0	0	0	0	1	1	0	0
297,500	0	297,500	11,356	1	0	0	1	0	1	0	0
380,429	3,500	383,929	9,828	1	1	2	4	0	10	7	3
2,382,199	814,882	3,197,081	319,423	7	29	35	50	33	71	26	10

Source: U.S. Environmental Protection Agency 1977.

operational procedures (Brown 1977).^{*} The majority of tanker emissions are escaping hydrocarbon (HC) vapors from on-board storage tanks and nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon monoxide (CO), and particulate matter from stack emissions during the offloading procedure. (The offloading procedure involves using a tanker's on-board engines at about 80 percent of full power to pump the crude to shore and lasts 10 to 12 hours for tankers in the 80,000 to 165,000 dwt class.)

Estimates based on the SOHIO project, a once-proposed major terminal for handling Alaskan crude (involving approximately 270 tanker visits per year), indicate that, on a yearly basis, SO_x emissions could range from 220 tons per year to 880 tons per year. The ranges are based on differences in the sulfur content (0.5 to 2 percent) of the fuel. If transit time in the port vicinity is included, the range would be from 500 to 2,000 tons per year. It is evident that requiring low sulfur fuel to be burned near or in port greatly reduces these emissions. Emissions of nitrogen oxides are estimated to range from 120 tons per year to 210 tons per year, again depending on whether transit time is included. Carbon monoxide and particulate emissions are minimal and are not expected to result in serious public health problems (Brown 1977). Particulates are estimated to be 40 tons per year and CO emissions have not been calculated.

The outstanding issue is that of hydrocarbon emissions which, with NO_x, are precursors for the formation of oxidants. Generally, most hydrocarbon emissions in or near port are associated with tankers not containing segregated ballast systems. Most of these vessels are small (less than 75,000 dwt in size). Because of their shallow draft, these small tankers are the only ships that can serve many U.S. ports (Table 13).

The operations of ballasting in non-segregated ballast tankers and tank cleaning (purging) both may involve the release of large quantities of hydrocarbons. For tankers with fully segregated ballast, no hydrocarbon ballasting emissions would occur. Similarly, if tank cleaning is not performed in port, no hydrocarbon effluents will occur. The range of hydrocarbon estimates is, therefore, extremely large, reflecting different assumptions as to the operations to be performed and the types of tankers. For the SOHIO project, the yearly estimates have run from essentially zero hydrocarbon emissions to as high as 10,000 tons per year. The lower figure represents

^{*}Additional information on the health effects of deep water ports is provided in the Transportation and Storage section of this report.

TABLE 13

CHARACTERISTICS OF MAJOR U.S. TANKER PORTS (1974)

Port	Maximum Draft Vessel Using Port (feet)	Maximum Tanker Size Provided For (dwt)	Crude Oil Handled (millions of bbls per day)	Oil Products Handled (millions of bbls per day)	Total Petroleum Handled (millions of bbls per day)
Under 50,000 dwt tankers					
San Francisco, Calif.	50	35,000	.21	.09	0.30
50,000-75,000 dwt tankers					
Boston, Mass.	41	50,000	.01	.20	0.21
Hampton Roads, Va.	47	50,000	--	.11	0.11
New York	46	55,000	.41	.73	1.14
Delaware Bay, Dela., Pa.	47	55,000	.87	.13	1.00
Baltimore, Md.	42	55,000	.02	.08	0.10
Houston, Texas	40	55,000	.09	.02	0.11
Galveston, Texas	40	55,000	.16	.01	0.17
75,000-100,000 dwt tankers					
Portland, Maine	47	80,000	.46	.03	0.49
Los Angeles, Calif.	54	100,000	.11	.02	0.13
100,000-150,000 dwt tankers					
Long Beach, Calif.	54	150,000	.14	.03	0.17
Puget Sound, Wash.	39	150,000	.14	.06	0.20

fully segregated ballast tankers and no release of hydrocarbons to the atmosphere from tank cleaning operations. The latter figure represents emissions that could occur if tank cleaning took place while in port and also along the coast near port. Table 14 compares the SOHIO estimated yearly emissions with emission rates that define new "major" air pollution sources--those that would be subject to emission offsetting requirements if they exacerbate a violation of a National Ambient Air Quality Standard. The State of California has been especially sensitive to these emissions as they would affect oxidant problems in southern California. In addition, all tanker stack emissions may contribute significantly to air quality degradation in or near ports.

The human health effects associated with photochemical oxidants (e.g., NO_x , SO_x) and airborne organics are not well understood, but it is known that photochemical oxidants in combination with specific airborne organics, such as the polycyclic aromatic hydrocarbons, have induced cancers and pulmonary adenomas (Stokinger and Coffin 1968; Laskin et al. 1970). Atmospheric oxidants also have been shown to initiate the carcinogenic action of this same class of hydrocarbons (Ayers and Buehler 1970; Altshuller and Beualini 1971). Thus, the development of offshore oil and gas reserves may result in atmospheric emissions that adversely affect public health.

In addition, potential adverse health effects may occur as a result of the separation of dissolved natural gas from crude oil. If separation occurs at the offshore production site, the working and nearby general population may be affected since toxic hydrogen sulfide (H_2S) may be associated with natural gas. The percentage of H_2S by volume of gas has been reported as ranging from 0 percent to 35 percent (Leggett and Williams 1979). If the gas is processed rather than flared, the toxic H_2S component must be removed. In addition to accidental release of gas prior to H_2S removal, another public concern involves disposal of H_2S after separation. An estimated 250 million ft^3 per year of gaseous SO_x or H_2S are vented to the atmosphere each year in the U.S. from flares and fugitive losses, assuming that natural gas contains 0.5 mole percent sulfur (Wilkins 1977).

Oil spills resulting from offshore oil and gas operations may also present public health problems. Potentially carcinogenic compounds, such as polynuclear aromatic hydrocarbons, are released during an oil spill. In a volatile state these may be inhaled, or as a liquid they may be concentrated in the body tissues of fin fish and filter feeding organisms such as clams and oysters near the spill. The nearby human population may be adversely affected by consuming the oil-contaminated marine biota which have incorporated these potentially carcinogenic compounds (IMCO et al. 1977).

TABLE 14

YEARLY EMISSIONS ESTIMATES
FROM ALASKAN CRUDE TANKERS AT PORT OF LONG BEACH

	EPA Guidelines ^a (tons/year)	Estimates from SOHIO Project (270 visits/year ^b)	
		Port Only	Port & Transit
Particulates	50	40	60
SO _x	50	220 ^c -880 ^d	500 ^c -2,000 ^d
NO _x	50	120	210
HC	50	0 ^e -7,000 ^f	0 ^e -10,000 ^f
CO	500	Negligible	

^aGuidelines for defining a "major" source in effect at the time of SOHIO (Alaskan crude) environmental impact statement review.

^bOnly large tankers considered (100 visits, 80,000; 73 visits, 120,000; 97 visits, 165,000).

^cAssumes a fuel sulfur content of 0.5 percent.

^dAssumes a fuel sulfur content of 2.0 percent.

^eNo ballasting or tank cleaning (purging) assumed.

^fBallasting and tank cleaning (purging) assumed.

Another obvious effect of oil spills is the loss of aesthetic resources due to oil residue on beaches. Deposits of tar and other petroleum residues, whether from oil spills or tanker cleaning operations, may present public health concerns. Acute toxicity may result from swallowing oil or, as mentioned, from inhaling petroleum fumes (National Academy of Sciences 1975). These problems tend to be local in nature, but may be significant in certain coastal urban areas.

The development of offshore oil and gas reserves is not expected to interfere, to any great extent, with public safety. However, accidents directly affecting oil and gas workers such as blowouts, toppling of platforms, and tanker collisions may also affect members of the general public who happen to be near the accident.

Summary of Research Needs

Health Effects Data

Some health effects data for the petroleum industry are reported for operations subject to OSHA recordkeeping requirements. The data include the number of employees, hours worked, recordable injuries and illnesses, incident rates for fatalities, and information on lost workdays and restricted activity. These data are reported by Standard Industrial Classifications (SIC; U.S. Office of Management and Budget 1972). With respect to drilling (SIC 1381) and exploration and production operations (SIC 1311), data from both onshore and offshore drilling rigs are commingled.

Onshore and offshore activities have diverged markedly over the last decade with respect to the nature and extent of risks. This is especially true as offshore exploration and production move into the deeper waters of the outer continental shelf.

An information gathering and reporting infrastructure is needed for separation of the data. More explicit data are also needed with respect to the nature and extent of illnesses and diseases. This information would be useful in retrospective epidemiological studies.

Offshore Platform Information Needs

From the above discussion it is evident, not only that more research is needed in the field of offshore drilling, but also that data collection activities should be streamlined. The U.S. Coast Guard has expressed its concern in this area by conceding that it is aware of a number of offshore oil and gas drilling companies with poor safety records, but a lack of documentation has prevented them from correcting potentially dangerous situations (Gillan 1980b).

More stringent and explicit OSHA regulations dealing with worker safety on offshore drilling rigs would also be required to investigate the risks involved in the offshore drilling industry. The specific areas that need attention are:

- o Offshore accident data should be segregated from onshore data.
- o Offshore drilling rig accident data should be segregated from accidents involving tankers and platforms.
- o More effective personnel and site-specific training programs should be devised.
- o Effective anti-drug programs should be instituted. (Most companies are doing it on their own. These programs should be screened and made mandatory for all companies involved in offshore drilling.)
- o Marijuana, unlike heroin and alcohol, leaves no telltale traces in urine. Experimental work is underway by American Medical Laboratories, Inc., involving the use of radioisotopes for identification, but such analyses are costly and time consuming and the results are uncertain. Low cost tests should be developed that will quickly detect the presence of marijuana under field (drilling or production platform) conditions.
- o Advanced research dealing with ocean bottom topography as related to pontoon anchors is needed.
- o Research dealing with ocean weather forecasting should be accelerated.
- o Research is needed in the design of safer, more reliable offshore drilling equipment. Of particular importance is the development of equipment that does not distract workers with undue noise.
- o Increased research in human factors engineering with respect to minimizing accidents in offshore development that are caused by human error.
- o Techniques should be devised for sharing U.S. knowledge and experience with relatively inexperienced countries.
- o Last, but not least, standardized accident reporting procedures should be instituted.

Concerned government agencies, industry, and trade associations should pool their resources and fund as much research as possible in these areas. As energy consumption rises, marine areas of the world are becoming prime exploration targets for the international oil industry. In 1976, 20 percent of the western world's crude production came from offshore areas, but currently over 30 percent of production is derived from beneath the ocean, largely in coastal waters. Since offshore drilling will be a major energy source in the years ahead, efforts should be made to make it as safe and efficient as possible. These efforts should include collecting detailed data and creating the infrastructure necessary for processing the information.

Effects of Drilling Muds

As is the case with onshore oil and gas development, a study is needed to define possible health effects associated with the use of drilling muds. Documentation is needed on the frequency and duration of worker exposures to the various formations of drilling muds. The study should include a retrospective epidemiological survey, possibly using data on workers in the Gulf Coast Basin, compared with bioassay information on the toxicity of various drilling muds, to assess the potential health risks. This information may be used to establish guidelines for handling and using drilling muds on offshore platforms.

Offshore Terminals

As oil and gas development moves farther offshore, complex terminals will be needed for production, storage, support, and/or loading and offloading. The effects that air emissions from such terminals have on occupational health and the health of the urban public are unknown. These are isolated sources of complex emissions, not subject to interactions with emission from other industries. In addition, the effect of possible transformation products from the interaction of these emissions and background environmental factors, including sea state and air-water interface conditions, should be explored.

Coastal Pipelines

As coastal oil and gas development expands, pipelines will need to cross coastal areas to deliver crude to storage areas or distribution systems. Techniques should be developed and tested to minimize the negative impact of constructing and maintaining these pipeline systems. Finally, agents should be developed to decrease the volatility of oil spilled from pipeline breaks and during offloading.

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ECOLOGICAL EFFECTS OF OFFSHORE DEVELOPMENT

Environmental impacts will result from developing offshore oil and gas resources. Concerns related to fish and wildlife and their habitats are most significant for large offshore oil and gas development projects, including exploration and production drilling, pipe-laying, and oil transfer and transport.

Exploratory Surveys

The actual operation of an offshore oil and gas survey vessel is similar to that of a commercial fishing ship. Thus, the vessels are not expected to harm the aquatic system. However, seismic surveying techniques--using contained detonations of a propane and oxygen mixture or high-powered oscillators to generate sound waves--may result in adverse impacts on resident or migratory biota.

Clark et al. (1978) wrote that seismic surveys offshore in deep waters do not affect living resources, if they are conducted as specified in established regulations. Before modern techniques were perfected, surveyors frequently used dynamite, which caused fish kills; however, modern seismic techniques have not caused any documented adverse impacts to living systems (Clark et al. 1978).

Experimental data on biological effects resulting from underwater explosions are summarized in Table 15. Mortality and injury of aquatic organisms depend primarily upon the charge weight, type of explosive, kind of organism, and the organism's proximity to the point of explosion. For example, a straight-line relationship was found between the percentage of fish fatalities and the distance from the charge (Chesapeake Biological Laboratory 1948). However, Fitch and Young (1948) reported an inverse relationship between injury to fish and the cube of the distance from the charge. They found that fish 10 feet from the explosion could receive about eight times the force of shock as those 20 feet away. Hubbs and Rechnitzer (1952) reported that, in contrast to high explosives, black powder explosions (charges between 20 and 45 pounds) in the bottom sediments, on the bottom surface, or near the water surface had no adverse effects on fish.

It generally has been accepted that fish with swim bladders are more vulnerable to underwater explosions than those without swim bladders (Alpin 1977; Crutchfield 1969; Young 1973). The data presented in Table 16 show that the swim bladder is by far the most vulnerable organ for striped bass, trout, and croakers.

TABLE 15
EFFECTS OF UNDERWATER EXPLOSIONS ON AQUATIC ORGANISMS

Weight of Explosive Used (lbs)	Type of Explosive Used	Distance from Blast and Pressure (lbs per square inch)		Major Aquatic Life Involved in the Experiment	Findings at Distances Indicated	Source
		Distance	Pressure			
10	60% petrogel	50	560	Fish	Fish with swim bladders were largely injured	Alpin 1947.
		55	509	Fish	Fish without swim bladders were largely uninjured	
40	60% petrogel	250	178	Fish	A few fish were injured up to the indicated distance	
20	60% petrogel	50	706	Spiny lobsters (<u>Panulirus interruptus</u>)	Lobsters were not injured	
		55	899			
200	60% gelatine dyanamite	50	1,520	Shrimp	Shrimp were not injured	Gowanloch and McDougall 1946.
200	60% gelatine dyanamite	200	380	Croakers (<u>Micropteron undulatus</u>)	Croakers were not injured	
800	60% gelatine dynamite	50	2,414	Shrimp	Shrimp were not injured	
30	TNT	100	404	Oysters	5% of oysters sustained fatal injury within indicated distance	Chesapeake Biological Laboratory 1948.
300	TNT	200	433	Oysters	5% of oysters sustained fatal injury within indicated distance	
30	TNT	200	202	Trout (<u>Cynoscion regalis</u>)	Injured at 200 feet; subsequent deaths due to injury occurred in generally decreasing proportions up to a radius of 500 feet (80 psi)	
				Striped bass (<u>Morone saxatilis</u>)		
3 x 30 (successive)	TNT	250	162	Striped bass	Increased the range of initial mortality from 200 to 350 ft	
3 x 30 (successive)	TNT	350	115	Trout	Increased the range of initial mortality from 200 to 350 ft	
300	TNT	150	580	Crabs	Lethal damage was limited to the indicated distance	
2,750,000	Unknown	2,640	690	Fish	Fish lethality was confined to an area of less than half a mile	Thompson 1958.
10	High explosive	160	175	Fish (Artic cisco and small <u>Coregonedes</u>)	Lethal damage to all fish within the indicated distance (equivalent to 25,450 sq ft)	Falk and Lawrence 1973.

TABLE 16

FREQUENCY OF REPORTED DAMAGE TO FOUR FISH ORGANS

Species	Organ			
	Swim Bladder	Liver	Spleen	Abdominal Vein
Rock (striped bass)	81 of 83 (98%)	11 of 83 (13%)	24 of 83 (29%)	33 of 83 (40%)
Trout	135 of 145 (93%)	20 of 145 (14%)	19 of 145 (13%)	92 of 145 (63%)
Croaker	12 of 13 (92%)	11 of 13 (85%)	6 of 13 (46%)	3 of 13 (23%)

^aIncludes all cases of fish injury.

Source: Chesapeake Biological Laboratory 1948.

Benthic organisms also may be damaged when an explosion takes place on the ocean floor. It is estimated that the disturbed area is approximately equal to twice the width of the crater (Young 1973).

Plumes, composed primarily of fine-grained sediments, accompany most of the explosions taking place on or in the ocean floor. It has been reported that the turbidity produced by underwater explosions in the West Cove near Cross Cay Island, Puerto Rico, decreases to a normal level of transparency within 2 hours after the blasts (Brown and Smith 1972). The explosives consisted of 4,000 pounds of C-4, which is 1.34 times more powerful than TNT on a weight-to-weight basis.

Searching for ways to minimize or eliminate harmful or irreversible environmental effects, several agencies have initiated firing programs. The Naval Ordnance Laboratory Field Branch (NOLFB), Solomons, Maryland, has performed underwater explosion tests since 1944 (Green and Davidson 1969). These experiments include tests with mines, torpedoes, depth charges, and phenomenological studies of special or new explosives. The laboratory uses three testing sites in the Patuxent River and one in the Chesapeake Bay. As a general rule, firings are prohibited in areas known to be favored fish habitats. For example, at the Patuxent River sites with a 40-foot water depth, firing is permitted during the entire year. In contrast, testing at shallower depths is permitted only between April and November. In the Chesapeake Bay, no firing is allowed during December, January, and February, and sometimes during March. These critical periods coincide with the maximum concentration of fish and, therefore, with maximum probable damage to them. The least probable damage would be caused by underwater explosions performed during June, July, and August, when fish are more dispersed.

Table 17 shows NOLFB data on mortalities resulting from underwater explosions between 1958 and 1972. In most instances, more nonedible fish than edible fish were killed during the experiments (most fish in the bay are not utilized for food). The average fish mortality (in pounds) per pound of explosive ranged from 0.698 in 1960 to 0.027 in 1972. The averages recorded between 1966 and 1972 were considerably lower than those for the previous period (1958 to 1965). This would indicate that, when a smaller amount of explosive is used per shot, the damage to fish can be substantially decreased.

Knowledge of the behavioral patterns of aquatic life is used in timing blasts to minimize impact. In addition, several methods have been suggested for driving fish away from the blast area. For example, radio broadcasts, pulsed electric currents, underwater sound, and underwater structures and lights are the methods most often used to attract fish to another location. Air bubble curtains, nets,

TABLE 17
FISH MORTALITY DATA^a

Year	Explosives Fired		Fish Killed			Average Mortality Relative to Explosions	
	Total Weight (lbs)	Number of Shots	Edible (lbs)	Non-Edible (lbs)	Total (lbs)	(lbs/shot)	(lbs/lb)
1958	19,000	44	613	7,107	7,720	175.0	0.406
1959	9,000	70	247	4,003	4,250	60.7	0.472
1960	22,000	65	807	14,553	15,360	236.0	0.698
1961	12,000	195	312	6,218	6,520	33.4	0.543
1962	14,000	45	561	2,069	2,630	58.4	0.188
1963	13,000	42	291	1,529	1,820	43.3	0.140
1964	16,000	82	290	5,070	5,360	65.4	0.335
1965	36,000	272	640	11,470	12,110	44.5	0.336
1966	34,000	53	556	2,304	2,860	54.0	0.084
1967	35,000	178	275	995	1,230	6.9	0.035
1968	42,000	209	1,200	100	1,300	6.2	0.031
1969	27,330	279	991	6,583	7,574	27.1	0.277
1970	17,107	151	1,036	1,064	2,100	13.9	0.123
1971	5,928	143	575	1,001	1,576	11.0	0.266
1972	18,505	70	170	337	507	7.24	0.027

^aData from the Naval Ordnance Field Branch, Solomons, Maryland.

Source: Young 1973.

chemicals, pulsed electrical currents, and radio broadcasts are commonly used to disperse or repel fish from the blast area.

In particularly hostile environments such as the Beaufort Sea and other areas of the Arctic Ocean, where it is difficult to obtain reliable acoustic measurements, it may be more environmentally desirable to use large dynamite charges to obtain good seismic readings. Repeated use of low intensity shocks by propane charges or electric oscillations to obtain good data may be more stressful on biota than a single large charge. This is an area which warrants additional research.

Exploratory Drilling

Offshore exploratory drilling operations for oil and gas are normally conducted from mobile platforms (e.g., barges, drill ships, jack-ups). The actual operation of the mobile unit is not expected to result in adverse environmental effects. However, impacts may result from the drilling process.

Direct environmental impacts, such as the removal of benthic substrate by floor sampling and coring, and the addition of drill cuttings and other discharges from the drilling rig to the ocean floor, may result in adverse effects on indigenous biota. The removal of benthic substrate or the addition of drill cuttings may result in the destruction of benthic organisms' habitats. In general, the addition of drill cuttings and other anthropogenic material will increase turbidity, eutrophication, and toxification of the aquatic system. These types of impacts may interfere with either indigenous organisms (e.g., plankton, benthos, fish) or migratory fish.

During any drilling operation, there is also the potential for a blowout to occur. Blowouts, which cause loss of control over the well, are extremely hazardous and would result in adverse effects on the ecosystem.

Drilling Muds

Exploration and well completion activities in the marine environment utilize drilling fluids or "muds" (Table 18). The use of these materials can result in a range of physical, chemical, and biological effects (Figure 11). The areas of greatest concern are that: the muds may be acutely toxic or may produce deleterious sublethal responses in sensitive marine species; and metals and organic compounds present in some drilling fluids may accumulate in marine organisms to concentrations that would harm marine life or human consumers of fishery products (Neff 1980; Richards 1979). Federal agencies and industrial interests have sponsored many laboratory and

TABLE 18
COMMON DRILLING FLUID COMPONENTS

Component	Primary Application
<u>Weighting Agents and Viscosifiers</u>	
Barite	For increasing mud weight up to 20 lbs/gal.
Calcium carbonate	For increasing weight of oil muds up to 10.8 lbs/gal.
Bentonite	Viscosity and filtration control in water-based muds.
Sub-bentonite	For use when larger particle size is desired for viscosity and filtration control.
Attapulgate	Viscosifier in saltwater muds.
Beneficiated bentonite	Quick viscosity in freshwater upper hole muds with minimum chemical treatment.
Asbestos fibers	Viscosifier for fresh- or saltwater muds.
Bacterially produced large organic polymer	Viscosifier and fluid loss control additive for low solids muds.
<u>Dispersants</u>	
Sodium tetraphosphate	Thinner for low pH freshwater muds.
Sodium acid pyrophosphate	For treating cement contamination.
Quebracho compound	Thinner for freshwater and lime muds.
Causticized quebracho	1-2 ratio caustic-Quebracho for thinning low pH freshwater muds.
Hemlock extract	Thinner for freshwater muds and in muds containing salt (10,000 to 15,000 ppm).
Modified tannin	Thinner for fresh- and saltwater muds alkalized for pH control.
Mined lignite	Dispersant, emulsifier, and supplementary additive for fluid loss control.
Causticized lignite	1-6 ratio caustic-lignite dispersant, emulsifier, and supplementary fluid loss additive.
Calcium lignosulfonate	Thinner for SCR and lime muds.
Modified lignosulfonate	Dispersant and fluid loss control additive for water-based muds.
Blended lignosulfonate compound	Dispersant, fluid loss agent, and inhibitor for RD-111 mud systems.

TABLE 18 (Continued)

Component	Primary Application
<u>Fluid Loss Reducers</u>	
Pregelatinized starch	Controls fluid loss in saturated salt water, lime, and SCR muds.
Sodium carboxymethyl cellulose	For fluid loss control and barite suspension in water-based muds.
Sodium carboxymethyl cellulose	For fluid loss control and viscosity building in low solids muds.
Sodium carboxymethyl cellulose	For fluid loss control in gyp, seawater, and freshwater muds.
Polyanionic cellulosic polymer	For fluid loss control and viscosifier in salt muds.
Sodium polyacrylate	For fluid loss control in calcium-free low solids muds.
Sodium polyacrylate	For fluid loss control in low solids muds.
<u>Lubricants, Detergents, Emulsifiers</u>	
Extreme pressure lubricants	Used in water-based muds to impart extreme pressure lubricity.
Processed hydrocarbons	Used in water-based muds to lower down-hole fluid loss and minimize heaving shale.
Oil dispersible asphalts	Used in water-based muds to aid in controlling heaving shale.
Oil soluble surfactants	Used for spotting around differentially stuck pipe.
Detergent	Used in water-based muds to aid in dropping sand. Emulsifies oil, reduces torque, and minimizes bit balling.
Non-ionic emulsifier	Emulsifier for surfactant muds.
Blend of anionic surfactants	Emulsifier for salt- and freshwater muds.
An organic entity neutralized with amines	Non-polluting lubricant for water-based muds.
Blend of fatty acids sulfonates, asphaltic materials	Used for spotting around differentially stuck pipe where weights in excess of 10 ppg are required.
<u>Defoamers, Flocculants, Bactericides</u>	
Aluminum stearate	Defoamer for lignosulfonate muds.
Sodium alkyl aryl sulfonate	Defoamer for saturated salt muds.

TABLE 18 (Continued)

Component	Primary Application
<u>Defoamers, Flocculants, Bactericides (Continued)</u>	
Flocculating agent	Used to drop drilled solids where clear water is desirable for a drilling fluid.
Paraformaldehyde	Prevents starch from fermenting when used in muds of less than saturation or alkalinity less than 1 cc.
Sodium pentachlorophenate	Bactericide used to prevent fermentation.
<u>Lost Circulation Materials</u>	
Fibrous material	Filler as well as matting material.
Fibrous mineral wool	Often used in areas where acids are later employed to destroy the material.
Walnut shells	
Fine	Most often used to prevent lost circulation.
Medium	Used in conjunction with fibers or flakes to regain lost circulation.
Coarse	Used where large crevices or fractures are encountered.
Ground mica	
Fine	Used for prevention of lost circulation.
Coarse	Forms a good mat at face of well bore.
Cellophane	Used to regain lost circulation.
Combination of granules, flakes and fibrous materials of various sizes in one sack.	Used where large crevices or fractures are encountered.
Blended high-fluid-loss, soft plugging material	One sack mixture for preparing soft plugs for severe circulation loss.
<u>Specialty Products</u>	
Shale control reagent	Calcium chloride mud for inhibiting the swelling of bentonitic shales.
Bentonite extender	Increases yield of bentonite to form very low solids drilling fluid.
Non-ionic surfactant	Primary surfactant for formulating surfactant muds. May be used in hot holes for viscosity stability.
Filming--amine	Corrosion inhibitor.

TABLE 18 (Continued)

Component	Primary Application
<u>Commercial Chemicals</u>	
Sodium chromate	Used in water-based muds to prevent high temperature gelation and as a corrosion inhibitor.
Sodium hydroxide	For pH control in water-based muds.
Sodium carbonate	For treating out calcium sulfate in low pH muds.
Sodium bicarbonate	For treating out calcium sulfate or cement in high pH muds.
Barium carbonate	For treating out calcium sulfate (pH should be above 10 for best results).
Calcium sulfate	Source of calcium for formulating gyp muds.
Calcium hydroxide	Source of calcium for formulating lime muds.
Sodium chloride	For saturated salt muds and resistivity control
Potassium hydroxide	For pH stability and inhibition.
Chrome alum (chromic chloride)	For use in cross-linking XC polymer systems.
<u>Oil Base and Invert Emulsion Muds</u>	
Invert emulsion (water in diesel oil)	Protects sensitive producing formulations.
Oil-based mud	Basically the same application as Ken-X.
Gelatinous oil-based fluid	For casing recovery, corrosion control, and protection of fresh water sands.
<u>Emulsifiers for Invert Emulsions</u>	
Primary emulsifier	Primary additives to form stable water-in-oil emulsion.
Viscosity and gel builder	Provides weight suspension.
High-temperature stabilizer	Improves emulsion under high temperature conditions.
High-temperature stabilizer	Improves emulsion, weight suspension, and fluid loss under high temperature conditions.

Source: U.S. Department of the Interior 1979.

Source: Adapted from Neff 1980; U.S. Department of the Interior 1979.

FIGURE 11
EFFECTS OF DRILLING FLUID DISCHARGED INTO
THE MARINE ENVIRONMENT

a few field studies to determine the nature and extent of these impacts. Research efforts are continuing, with activity concentrated in the Flower Garden Banks area of the Gulf Coast and the Georges Bank areas of the North Atlantic.

Laboratory Studies

Most laboratory studies related to drilling muds have been sponsored by the oil industry and by the Federal government, with a concentration of research effort at the U.S. Environmental Protection Agency's Environmental Research Laboratory at Gulf Breeze, Florida. Several general reviews of the status of laboratory research have been presented (Ayres 1980a; Neff 1980; Richards 1979). A number of recent studies were discussed at a symposium held in January 1980 (Steering Committee for the International Symposium on Drilling Fluids and Cuttings, in press). A complete review of all laboratory or controlled ecosystem studies on the effects of drilling fluid discharges has been sponsored by the National Oceanic and Atmospheric Administration (NOAA) in association with program effects on the Lower Cook Inlet of Alaska. A draft version of this report was scheduled for completion in October 1980 (Calder 1980).

Most of the laboratory studies on drilling fluid effects have involved the use of standard, 96-hour static bioassays to determine acute lethal toxicity. Testing has been undertaken using individual drilling fluid components and whole drilling fluids. A variety of test organisms have been used, including both freshwater and marine species. In general, these studies have found that most whole drilling fluids are "practically non-toxic," based on the classification scheme presented by Sprague (1973). However, some researchers, notably Richards (1980) and Conklin et al. (1980),* reported bioassay results indicating that some drilling fluids may be highly toxic.

Fewer laboratory studies have been conducted to determine the sublethal effects of drilling fluid discharges. Ayers (1980a) notes that, in most studies, sublethal effects occurred at concentrations above the 100 to 1,000 ppm range. Bioaccumulation of certain drilling fluid constituents (barium, chromium) has been documented, with depuration occurring in some cases but not in others (Brannon and Rao 1979; Liss et al. 1980; Page et al. 1980). Recent efforts also have included investigations of sublethal effects on corals (Shinn et al. 1980; Thompson 1979; Thompson and Bright 1977), and on

*Neff (1980) reported that the drilling fluid used in this study was a highly treated composition not intended for marine disposal.

bivalve molluscs (McLeod et al. 1980). These studies generally indicate that effects are highly variable, depending upon the species studied, drilling fluid characteristics, and environmental conditions.

Field Studies

Several field studies have been conducted in the major U.S. oil and gas lease sale areas to determine the fate and effects of drilling fluid discharges in the marine environment. Sponsored mainly by the Bureau of Land Management (BLM), the oil industry, and most recently through the Federal Interagency Energy/Environment Research and Development Program, these studies range in complexity from diver observations to detailed monitoring of water column and benthic effects.

The major studies include:

- o Tanner Bank Mud and Cuttings Study, which was carried out at a Shell Oil Company exploratory drill site about 160 kilometers west of Los Angeles, California, and included analyses of drilling fluid plume dispersion, effects on water, and local bottom sediment chemistry (Ecomar, Inc. 1978; Ray and Meek 1980; Meek and Ray 1980).
- o Lower Cook Inlet Study, which was carried out at an Atlantic Richfield Company site about 56 kilometers west of Homer, Alaska, and included discharge dilution tests using a fluorescent dye, on-site bioassay testing, and bottom sediment sampling (Dames and Moore 1978).
- o Mid-Atlantic Monitoring Program, which was carried out at an Exxon drilling site about 156 kilometers east of Atlantic City, New Jersey, and included pre-drilling, drilling, and post-drilling monitoring of water chemistry, bottom sediments, and benthic communities (Ayers et al. 1980; Mariani et al. 1980; Menzie et al. 1980).
- o Maximum Mud Discharge Study, which was carried out at an Exxon drilling site about 80 kilometers south of Cameron, Louisiana, and included intensive discharge plume monitoring at several depths (Ayers 1980a), accompanied by the use of a computer model to predict the short-term fate of the material (Brandsma et al. 1980).
- o OCS Rig Monitoring Program, sponsored by BLM at various drilling site locations, which includes examinations of bottom topography, plume dispersion, and effects on bottom sediment

conditions (Alexander et al. 1977; Bright and Rezak 1978a; Bright and Rezak 1978b; Groover 1977; Tillery 1980).

A review of these studies by Ayers (1980a) concludes that: (1) drilling fluids have a minimal local effect on ocean water quality, since they are dispersed rapidly and diluted within the area of the production field; and (2) effects on the benthic environment are localized and temporary. Richards (1979) notes that such conclusions have not been substantiated since most of the field studies have not been published in peer review journals. Careful review of these studies is an objective of the previously mentioned NOAA study that is underway.

Production Drilling

Production drilling is similar to exploratory drilling; however, it continues for a longer period of time and more drilling occurs at a single site. Therefore, there is a larger quantity of drill cuttings and mud to be disposed of. When this material is deposited overboard, the bottom topography is altered and benthic organisms may be smothered by silts and sediments. This disposal practice may result in increased turbidity, eutrophication, and toxification of local waters. In addition, the increased activity (e.g., noise from compressors) from boats, pumps, and other equipment associated with production drilling affects fish and other wildlife. Some species avoid an area that could have been occupied for feeding or reproduction, while other species are attracted to such activity.

As with exploratory drilling, the potential for blowouts exists and could lead to adverse impacts on the local environment and biota. Oil spills also would result in adverse environmental effects. This topic will be discussed in the following sections; however, it should be noted that spills are likely to occur prior to pipeline construction during the transfer of oil between production platforms and tankers or barges.

Pipelines

Adverse environmental impacts may be realized as a result of any of the following pipelaying processes: underwater excavation or dredging, subsea burial, corridor routing, and pumping station or landfall construction (Clark et al. 1978). The environmental effects of underwater excavation or dredging will probably be quite similar to the effects resulting from drilling operations. It is anticipated that the removal of benthic substrate during the excavation process will result in the loss of habitat for indigenous benthic organisms. The removal of substrate and the subsequent burial of pipeline will involve increased activity in the area. This type of environmental

disruption could affect both indigenous and migratory biota; areas occupied for feeding, reproduction, and migration; and niches for other activities. Increased turbidity and sedimentation resulting from excavation and burial may also adversely affect biota.

Corridor routing through sensitive habitats or pipelaying in wetlands may result in both physical and biological impacts. Natural drainage and current patterns will be disrupted and erosion of soft and unconsolidated sediments in marshland areas may be markedly accelerated (Council on Environmental Quality 1974). This type of disturbance of the marsh environment may lead to changes in ambient turbidity, salinity, acidity, hydrogen sulfide toxicity, and biological oxygen demand.

Pipeline canals that are adequately backfilled or plugged may have temporary, localized effects on circulation patterns in marshes, but they do not result in permanent, continuous canals and spoil ridges. Water movement patterns remain essentially unchanged following restoration procedures. The effects of staggered borrow pits and discontinuous spoil deposits are localized and relatively small. Of greater significance to the hydrological regime of the brackish marsh are: the construction of leveed access roads, the dredging of access and pipeline canals, and subsequent spoil deposition. Leveed roadways and open canals bordered by continuous spoil levees generate a complex of interactions which may facilitate changes in the marsh's freshwater sheetflow from the uplands and facilitate rapid marsh drainage. The result may be a lower water table under the affected marsh surface, and eventually, drier conditions in high marsh areas (Longley and Jackson 1980).

Tankers and Barges

The actual operation of oil-carrying tankers or barges is not expected to result in adverse environmental effects. The effects would be similar to those resulting from the operation of any sea-going vessel (e.g., commercial fishing ships). However, oil spills may occur during the transfer of oil between production platforms and tankers or barges.

Environmentally harmful impacts may result from tank cleaning and deballasting operations which are required when: a cargo is to be carried that will not tolerate residues from a previous cargo, a vessel is to undergo repair work, and clean ballast is to be taken on board (Clark et al. 1978). In the process of tank cleaning, the cleaning water sprayed into the dirty tanks will dislodge much of the oil adhering to structural members. Pumping this directly overboard will result in significant oil discharges. This practice is restricted by recent legislation limiting the quantities of oil

pumped overboard (Clark et al. 1978). An emerging practice is to utilize the crude oil itself as a pressure spray to clean tank walls. This minimizes the amount of water and detergent needed in the cleaning process.

The "load on top" technique recently adopted by industry reduces the amount of oil discharged to within the permissible limits of the present law (Clark et al. 1978). With this technique, oil residue from the tank cleaning operation is pumped into an empty cargo tank. The mixture is then allowed to separate by gravity (the oil is normally on top since its density is lower than that of water). Water is pumped overboard until the interface approaches the suction line. The remaining fluid--a mixture of about 75 percent oil and 25 percent water--is transferred to a cargo tank in which new oil is loaded on top. Effective oil/water separation may be adversely influenced by the following: severe sea state conditions, insufficient separation periods due to a short voyage, agitation due to the pumping operation itself, oil with a specific gravity close to that of seawater, inaccurate overboard discharge measuring devices, and human error (Clark et al. 1978). The adverse effects resulting from the discharge or spillage of oil will be discussed in the section below on oil spills.

Offshore Storage

As with pipelaying operations, adverse environmental effects may be realized from the construction of subsea storage facilities. Severe bottom currents may initiate ruptures in these systems, leading to oil contamination of seawater adjacent to the storage site. In addition, there is the potential threat of spills during oil transfers.

Oil Spills

The entire sequence in the development of offshore oil and gas reserves carries with it the potential for oil leaks and oil spills. The release of oil to the environment may result from blowouts or natural seeps during the drilling, well completion, or production processes; from the transfer of oil from platforms to tankers or tankers to storage facilities; from oil pipeline leaks; or during tanker washing or ballasting operations. Between 1971 and 1975, an average of 18.4×10^9 gallons of oil per year was reportedly spilled in U.S. waters (Council on Environmental Quality 1976).

Several policies have been initiated by the Federal government to prevent accidental oil spills (Brown 1977). In addition, methods are being developed and tested to contain and remove oil slicks. However, a correlation between the quantity of oil spilled and the

level of oil imports and offshore drilling can be expected to continue.

An oil spill can harm wildlife that ingests petroleum or loses the insulating capacity of its feathers or fur. Oil spills have drastic implications for oceanic and diving birds (Clark et al. 1978). Generally, fish are able to avoid the effects of an oil spill because they can swim beneath it.

In addition to direct kills of organisms, the major adverse environmental effects of direct oil pollution of coastal waters are: disruption of feeding and reproductive activities of aquatic species; changes in physical and chemical habitat, causing exclusion of species and reduction of populations; and stresses on the ecosystem from decomposition of liquid effluents, resulting in altered productivity, metabolism, system structure, and species diversity (Clark et al. 1978).

The effects of oil spills are complex, whether from tankers, platforms, or terminals. Some of the major components of fish and wildlife species and habitats that are affected include (Clark et al. 1978):

- o Endangered birds. The known and suspected coastal foods of the American peregrine falcon, southern bald eagle, osprey, and other birds are sensitive to oil spills in any season.
- o Migratory waterbirds. Areas along the shore have been identified as having significant concentrations of migratory birds during the winter, spring, and fall.
- o Shellfisheries. Areas along the shore have been identified as beds for surf clams, bay scallops, northern hard clams, oysters, and others. Both commercial and sports harvesting areas for these species would be affected in any season.
- o Coastal finfish. A 25-mile strip of coastal waters along the entire length of the shore has been identified as critical during the summer and fall with respect to the egg and ichthyoplanktonic stages of the scup, porgy, menhaden, and other species.
- o Estuarine finfish. Estuarine areas and sounds have been identified as important areas for weakfish, sea trout, whiting, striped bass, and other fish during the spring, summer, and fall.

- o Wetlands. All marsh areas have been identified as sensitive in any season.
- o Wildlife refuges and management areas. All national wildlife refuges, wildlife management areas, wildlife areas, and natural areas have been identified as critical in any season.
- o Beaches with high-intensity use. National recreation areas, including adjacent state and municipal beaches, have been identified as areas of high intensity usage in any seasons.
- o Parks and recreation areas. The locations of all state parks and national recreation areas have been recorded as important in any season.

Marine oil spills have involved both crude and refined oils (mostly no. 2 fuel oil). Crude oil contains water soluble components that are somewhat toxic to marine organisms, while no. 2 fuel oil is highly toxic (Bell 1971). Spilled crude oil is altered by weathering which involves evaporation, dissolution, microbial decomposition, and chemical oxidation. The processes of evaporation and dissolution lead to rapid depletion (in 2 to 4 days) of the low boiling, highly toxic fractions in an oil slick. Microbial and chemical oxidation of most higher boiling fractions is a relatively slow process and may take several years (Moore et al. 1973). Refined oils contain a greater percentage of low boiling substances and, therefore, are more toxic than crude oils. As an example, a no. 2 fuel oil spill at West Falmouth, Massachusetts, produced a massive, immediate kill of fish, clams, snails, crabs, lobsters, worms, and other invertebrates (Blumer and Sass 1972). Oil was incorporated into sediments and continued to inhibit repopulation 9 months after the spill. Normal functioning of benthic communities was profoundly affected for years after the spill (Jacoff 1979).

It is important to understand the fate of oil discharged or spilled in the marine environment. Rates for microbial degradation of oil components and the role of photochemical reactions in altering or destroying the compounds must be identified and quantified in order to accurately predict the effects of oil spills on biota.

Thus, a large oil spill with a low recovery rate could be deleterious to aquatic fauna and flora. The degree of impact would be contingent upon the amount and type of oil spilled and upon the extent of aquatic biota present. Should such a spill occur in a warm estuarine or marine area, the following general effects may occur:

- o Direct lethal toxicity. Dissolved aromatic hydrocarbon derivatives could disrupt membrane activity in crustaceans

and burrowing organisms and to a lesser extent in fish and mollusks, causing deaths (Moore 1973).

- o Disruption of physiological and behavioral activity. Chemical communication is inhibited, leading to abnormal feeding, reproduction, orientation, and/or migration of marine organisms (Moore et al. 1973). In the case of most spills, this effect would persist at most only a matter of a few hours if it occurred at all. However, in certain rare instances, this effect could persist for several months, and in the most extreme case, for a year or more. This would be true if a highly toxic product such as no. 2 fuel oil spilled in unusually turbulent seas so that vertical mixing occurred and the sediments became saturated with the oil (Straunghan 1972).
- o Direct coating by oil. Oil may smother or physically inhibit activities such as feeding and locomotion. Sessile organisms are most susceptible to coating.
- o Incorporation of hydrocarbons in food chains. Polynuclear aromatic hydrocarbons, some of which are carcinogenic, are present in oils generally in the range of a few parts per million. These components are easily absorbed and concentrated by marine animals. However, such marine animals quickly depurate these hydrocarbons once they have been removed from exposure (Anderson 1973; Battelle Pacific Northwest Laboratories 1973). Fin fish and filter feeding organisms such as clams and oysters concentrate hydrocarbons in body tissues, creating an objectionable taste.
- o Habitat changes. Alteration of the physical-chemical environment, especially in the sediment, will cause shifts in the number and kinds of species present. The degree to which oil contaminates sediments is a function of the absorptive capability of the sediment, depth of the water, vertical mixing, and the degree to which the slick has weathered and become more dense.

The acute biological effects of oil pollution, such as mass mortalities, require immediate remedial measures. However, the sublethal effects of persistent toxic substances or compounds that degrade to toxic substances on benthic organisms should be determined (Goldberg 1978). Since petroleum compounds have shorter residence times in water than in sediments, benthic organisms are subjected to greater exposure than pelagic organisms.

Summary of Research Needs

The study of the effects of oil spills has received a great deal of Federal attention in the past decade. Current research focuses on monitoring long-term effects and on the recovery and enhancement of coastal wetlands affected by oil spills. Federal involvement in the oil spill arena has moved from the study of basic effects to regulatory control. The state of knowledge is diverse and in-depth, as indicated by the above discussions and voluminous reports on the subject. This section focuses on a few unresolved research problem areas.

Effects of Drilling Muds

As noted above, a variety of laboratory and field studies have been carried out on the effects of drilling fluid discharges in the marine environment. However, insufficient coordination of research efforts, attended by variability in experimental design and research results, has led to a lack of consensus on this issue. Thus, there is a crucial need for more efficient planning and management of research to identify and resolve the major questions pertaining to the nature of drilling fluid discharges, their transport and transformation, fate, and effects in the marine environment. As detailed below, each of these major research areas involves several specific research objectives.

Description of Drilling Fluid Discharges

It is well known that the composition of drilling fluids is highly variable (Petroleum Equipment Suppliers Association 1980), and that the toxicity of additives varies (Ayers 1980a). This undoubtedly accounts for much of the variability in the results of standard bioassay testing. Several recently initiated efforts will address some aspects of this research area:

- o One objective of a literature survey being conducted under NOAA's guidance is to synthesize available information on the composition of drilling fluids and their use by the petroleum industry (Calder 1980).
- o Several studies involving the chemical analysis of drilling fluid samples are being sponsored through EPA's Gulf Breeze Laboratory (U.S. Environmental Protection Agency 1980).

However, a more complete characterization of the range of chemical compositions in use is required. In addition, information is needed on the total volumes of the various types of drilling fluid discharges, the geographical distribution of these discharges, and methods of discharge.

Fate and Transport

Many of the field studies that have been conducted have addressed the short-term transport and fate of discharged fluids. Fewer studies have been conducted on long-term fate and transport. Due to the diverse oceanographic conditions of areas being drilled, it is difficult to form generalizations based on the available studies. Recently initiated research efforts are expected to meet some of the major information needs related to fate and transport. These studies include:

- o A second objective of the literature survey being conducted under NOAA's guidance is to synthesize available information on the fate of drilling muds and cuttings in the marine environment (Calder 1980).
- o The Bureau of Labor Management plans to sponsor an overview of its past rig monitoring efforts (Burke 1980).
- o Two major projects, the Interagency Research and Monitoring Program on the Flower Garden Banks (Burke 1980) and the Interagency Biological Task Force Monitoring Program for Georges Bank lease sale 42 (Bolton 1980) will include field studies on transport and fate.
- o The oil industry will continue to sponsor research such as the long-term study planned as part of Exxon's Mid-Atlantic Monitoring Program (Ayres 1980b).

In conjunction with these planned research projects, there is a need to delineate the differences between physical effects in low-energy environments and those in high-energy environments. To fill specific information gaps, additional research may be needed on plume behavior, the dispersion of drilling fluid constituents within the water column, and accumulation and long-term transport of settleable fractions. Additional field studies may also be necessary to identify any undesirable chemical transformations of drilling fluid constituents that may result from weathering processes. Also of importance is the continued development, application, and verification of predictive models. Computer simulations, such as the model developed by Brandsma et al. (1980), can provide valuable guidance based on limited data (e.g., current structure, density profile, discharge, and drilling fluid characteristics).

Biological Effects

A major area of controversy has been the effects of discharged drilling fluids on marine communities. Difficulties have been

encountered in the interpretation of bioassay results, in relating laboratory data to field data, and in assessing the limited information pertaining to any potential long-term effects. A broader question involves formulating a conceptual approach to predicting effects in different types of ecosystems or ecotypes (e.g., Gulf of Mexico, Mid-Atlantic, Northern Pacific).

Recently initiated research efforts should contribute substantially to an understanding of the biological effects of discharged drilling fluids. Key efforts include:

- o A third objective of the literature survey being conducted under NOAA's guidance is to synthesize available information on the biological and ecological effects of drilling fluids (Calder 1980).
- o Continued acute toxicity and sublethal effects testing efforts on drilling fluid samples are part of the research program at EPA's Gulf Breeze Laboratory (U.S. Environmental Protection Agency 1980).
- o Two major projects, the Interagency Research and Monitoring Program on the Flower Garden Banks (Burke 1980) and the Interagency Biological Task Force Monitoring Program for Georges Bank lease sale 42 (Bolton 1980) will include field studies related to biological and ecological effects (e.g., determining baseline conditions, trophic transfer of drilling fluid constituents, and effects on community dynamics).

In conjunction with these planned research projects, research must focus on: standardization of bioassay methods for lethal and sublethal effects, and the selection of appropriate test organisms; undertaking field investigations to verify laboratory findings; determining the physical impacts of mud discharges (e.g., burial, habitat alteration); and determining the areal extent of impacts. Additional research should be directed toward identifying any potentially adverse effects on commercially important species. Over the long-term, the development or adaptation of ecological models may allow the synthesis of existing information for application in new drilling locations.

Effects of Seismic Testing

As discussed above, there is a controversy over whether it is environmentally advantageous to utilize a number of low-energy intensive seismic shocks in offshore oil exploration or a single large explosion, such as that propagated by dynamite, to obtain sufficient readings. This controversy is particularly relevant to

hostile marine environments or sea-state conditions. Additional information is required focusing on behavior and mortality of marine biota exposed to repeated low-level seismic shocks.

Cumulative Effects

Habitat disturbance and the effects of drilling fluids are beginning to be studied with respect to offshore platforms. These field studies are largely directed toward a single platform and a single impact. Research is needed which will focus on the cumulative effects of large-scale development over a wide area (e.g., Georges Bank, Gulf of Mexico, Gulf of Alaska).

Overall large-scale programmatic studies have been conducted (e.g., Gulf of Alaska). These have largely focused on the characterization of indigenous biota, migration patterns, and bioassay analyses. Additional attention should be placed on the interaction of offshore subsea and fixed platforms, their effects on the fauna inhabiting contiguous areas, and resultant long-term impacts. Attention may need to be placed on spacing platforms to avoid environmental degradation and on habitat reclamation.

Effects on Deep Water Environments

With fixed offshore production platforms operating in as much as 1,025 feet of water (Gulf of Mexico) and mobile rigs in water as deep as 4,876 feet (205 nautical miles east-northeast of St. John's, Newfoundland), offshore drilling technology is entering a new era. Sea floor completion systems will begin to replace fixed platforms. With such a development, fauna inhabiting the deep ocean floor of the continental shelf and trenches will be disturbed. The potential effect of offshore development on these forms is relatively unknown. Many of these species have evolved in an environment that is relatively stable in terms of temperature, chemistry, and physical character and topography of sediments. More research is needed to fully characterize the impact of offshore development on fauna of the deep areas of the continental shelf.

Impact of Natural Seeps

For many years marine geologists have been aware of numerous active and quiescent seeps discharging into the environment. These include discharges of gas as well as oil. These seeps have important exploration implications.

Natural seeps have been observed in waters of the continental shelf off shore from California, Texas, and Louisiana. As much as 10 percent of all oil entering the marine environment is attributed to

such seepage (Albright 1973; U.S. Environmental Protection Agency 1978).

In determining the cumulative impact of spilled crude oil on the marine environment, the contribution of oil from natural seeps must be assessed. Also, these seeps should be utilized to determine long-term chronic effects and the long-term adaption of marine biota to oil contaminated sediments.

TRANSPORT AND TRANSFORMATION

This section describes the movement and possible transformations of pollutants associated with offshore oil and gas operations in both atmospheric and aquatic environments. Observable discharges such as oil spills and drilling fluid effluents are discussed; however, future research emphasis should be placed on the fate and transformations of atmospheric emissions that reach the marine environment.

Atmospheric

The extent of airborne transport of offshore oil and gas pollutants is a function of both the physicochemical characteristics of the emissions and any extraneous airborne conditions and elements acting upon them. The interaction of these factors will determine how and to what extent emissions are transported. Complex chemical transformations between atmospheric emissions, various constituents, natural background levels of airborne chemicals, and anthropogenic pollutants may result in pollutants differing from those initially emitted from offshore oil and gas operations.

The chronic loading of atmospheric emissions to the surrounding marine environment by both wet (i.e., rain) and dry deposition presents a potentially serious impact. It is important to realize that these emissions occur for the duration of offshore oil and gas operations. Unlike an oil spill, there are no methods for "after-the-fact" treatment and cleanup of atmospheric emissions.

Pollutants resulting from atmospheric emissions can settle on the surface film of the open ocean near the vicinity of offshore oil and gas operations. These pollutants are subject to chemical transformation and may also reach and remain in the water column, settle into bottom sediments, or be transported into other areas. In the open ocean, the surface and the upper reaches (50 m from the surface) are extremely important to primary production, which is essential for the support of all other life forms (e.g., zooplankton, crustaceans, fish). Therefore, the extent and effects of atmospheric emissions from offshore oil and gas operations should be investigated with respect to such impacts.

Aquatic

Oil discharged on the ocean surface undergoes physical, chemical, and biological alterations. Rapid physical and chemical processes include (McAuliffe 1977):

- o Spreading and movement with wind and currents;

- o Evaporation of the volatile components;
- o Solution, emulsification, and dispersion of small droplets into the water;
- o Sedimentation;
- o Spray injection into the air; and
- o Chemical oxidation.

The transport and fate of oil is variable and influenced by conditions, such as location, winds, waves, currents, water depth, temperature, salinities, organisms, nutrients, and kind of oil (McAuliffe 1977). When added to calm waters, most oils spread in a thin, continuous layer that forms a circular pattern. As the oil slick expands in size, it is not uniform--thicker patches within the slick appear (McAuliffe 1977).

Crude oils and petroleum products may contain appreciable amounts of nitrogen, sulfur, and oxygen-containing compounds, some of which are surface-active. These compounds and their concentrations determine the formation of oil-in-water droplets or water-in-oil masses on the surface. The general tendency is to form water-in-oil emulsions. However, under agitation by wind and waves, many oils break up, and small droplets disperse into the underlying waters (McAuliffe 1977). Such dispersion may be assisted by bacteria-produced, surface-active compounds (Boehm and Quinn 1973), or by oil attachment to particulate matter in water.

Some crude oils have a tendency to form water-in-oil emulsions, frequently referred to as "chocolate mousse." These emulsions ultimately may become pelagic tar (tar balls) that strand on beaches. However, crude oil spills probably contribute a minor amount of oil appearing as tar balls. Much of the tar stranded on beaches originates from washing tanker compartments, as evidenced by the viscous oils or waxy materials bound with sediment (McAuliffe 1977). As surface slicks break into oil droplets or particles and disperse in near-surface waters, most remain suspended (Brown and Huffman 1976) and move with the water. Some oil does sink, apparently through association with inorganic mineral matter suspended in water (McAuliffe et al. 1979).

The first compositional changes in oil spilled on water involve evaporation and solution of volatile components. These processes are simultaneous and competitive (McAuliffe 1977). The rates and extent of these changes depend upon the chemical and physical nature of the

oil, wind velocities, sea states, and water temperature. Each volatile hydrocarbon will evaporate and also go into solution at rates that depend upon its vapor pressure (American Petroleum Institute 1953) and solubility (Button 1976).

Oil discharged on a water surface is not in equilibrium with reference to evaporation and solution of hydrocarbons. Wind constantly renews the air over the slick, and water movement (waves and currents) renews the underlying water. Hydrocarbons that dissolve in water evaporate quickly (McAuliffe 1977).

Concurrent with physical and chemical alterations are biological processes that operate most effectively after the physical processes have been initiated. Biological processes include degradation by microorganisms, and uptake (if exposed) by larger organisms, followed by excretion, metabolism, or storage (McAuliffe 1977).

The rate of microbial degradation (e.g., bacteria, yeasts) will depend on many factors such as temperature; the concentrations of nitrate, phosphate, and dissolved oxygen in the water; the presence of other organic compounds; and an area's history of previous exposure to oil (Farrington 1977).

A basic understanding of the various transfer pathways and fates of oil has been derived from laboratory studies, field studies, and the application of existing scientific knowledge (Farrington 1977). These potential pathways and fates are represented in Figure 12. Farrington (1977) identifies the following fundamental questions:

- o What portions of oil inputs follow each of the various pathways of transfer?
- o What are the rates of biochemical and chemical degradation of whole oil and components of oil during the various stages of movement through the marine environment?
- o What are the final rates of oil removal by biochemical and chemical degradation, and by deep burial in sediments?

It is important to realize that these questions cannot be satisfactorily answered.

Unlike atmospheric deposition of pollutants, there are methods for treating and cleaning up oil spills. Farrington (1977) provides the following evaluation of oil spill cleanup methods.

The use of nontoxic emulsifiers of dispersants on an oil spill would result in increased dissolution of the oil

Source: Farrington 1977.

FIGURE 12
FATE OF OIL SPILLS

and accommodation into the water column, adsorption into particulate matter, and incorporation into sediments. On the one hand, this might further the biodegradation of the oil by increasing mixing of oil, nutrients, oxygen, and naturally occurring microbial populations capable of degrading the oil. On the other hand, it would spread oil throughout the water column and sediments, possibly increasing the extent and severity of the toxic effects on organisms. The incorporation of significant quantities of oil into sediments could prolong the exposure of an area to the oil and adversely affect bottom dwelling organisms. Resuspension of the sediment and transport to other areas would increase the size of the affected area. The use of sinking agents to remove the slick from surface waters would also result in the incorporation of the oil into sediments, which may not be advisable.

In addition to oil, there are other substances used during offshore drilling operations that might reach the aquatic environment. Drilling muds, cuttings, and formation water and its dissolved, emulsified, and suspended solids are normally discharged to the surrounding aquatic environment during exploratory and development drilling.

Currently, little is known about the transport and transformation of drilling fluids. This is not surprising considering the chemical complexity of drilling fluids, the diverse geographical conditions of areas being drilled, varying oceanographic conditions, and the fact that little is known about the basic biology of marine systems. Richards (1979) identifies a research study which showed that a near-surface discharge of drilling fluid did not disperse uniformly, but concentrated above the thermocline. Therefore, the potential for direct and/or indirect drilling fluid exposure via thermocline transport should be investigated under different hydrographic regimes.

Summary of Research Needs

- o Information is needed on the extent and effects of the deposition (wet and dry) of atmospheric emissions from offshore oil and gas operations. Emphasis should be placed on hydrocarbon species and their effect on surface films.
- o The air-sea interface should be characterized, particularly with respect to intermedia transfer via resuspension (airborne) of evaporative hydrocarbons.
- o Information is needed on the role of emulsified oil in terms of persistence, transformation products, and ultimate sinks.

- o Characterization is needed of transport and transformation of oil under deep sea pressures and chemical redox conditions.
- o Information is needed on the long-term degradation of and ultimate products from the breakdown of drilling fluids in the marine environment. Research should focus on entrapment of pollutants adjacent to the deep sea floors of the continental shelf and the merits of surface versus subsurface discharge of drilling fluids.

Part 4

Refinery Operations

Informational Needs

REFINERY SUMMARY

In discussing health research needs related to refinery activities, this section focuses on occupational and public health as it may be affected by exposure to airborne and surface-condensed toxic hydrocarbons. A voluminous amount of relevant data is available in the public domain. Much additional data exists as proprietary information relevant to catalysts, process chemicals, and in-plant, company sponsored emissions and ambient monitoring studies. An intensive effort is needed to bring all of this information together and conduct a rigorous, well defined risk assessment.

Several reports have appeared recently concerning large numbers of brain tumor deaths among workers at Gulf Coast petroleum refineries and petrochemical complexes. A recent mortality study of refinery workers in the United Kingdom found no significant increased risk for brain cancer, but researchers noted an above normal incidence of malignant melanoma (skin cancer), esophageal, stomach, intestinal, and rectal cancers. Research is needed, especially epidemiological studies, to determine the extent and cause of these occupational illnesses.

Many persons other than full-time refinery workers, such as contractor employees, construction workers, part-time employees, railroad workers, and truck drivers, work within the boundaries of a refinery complex and may be exposed to hazardous chemicals. Normally, data collection with respect to morbidity and mortality studies does not include these workers. A reporting mechanism should be developed for the refinery industry which will include these individuals.

Dermal contact is a primary mechanism for exposure to hydrocarbons by refinery workers. A number of studies are needed to quantify this problem. These should include the development of a method for detecting polynuclear aromatic hydrocarbons on skin that is safer than using ultraviolet light.

This section notes that there are several research needs associated with occupational health. Studies are proposed as needed in the areas of biological monitoring, epidemiology, and bioassays.

In addition, research concerning public health should be conducted. Incidences of diseases in communities adjacent to petroleum refineries should be assessed and significant variations from the norm should be followed by in-depth investigation. Sources of information for review should include registries of prevalence of cancer, heart disease, birth defects, and neurological disorders.

Research regarding ecological effects should focus on the effects of airborne ethylene and phenols on the growth of natural flora and crops, especially with respect to growth rate reduction, premature abscission, and breaking dormancy. More intense research should be conducted on the use of oily wastes in landfarming. Moreover, the roles of hydrogen chloride and hydrogen fluoride should be defined. Emitted from refineries, these chemicals may have effects on the formation of acid rain, as well as other impacts on the ambient environment.

Low concentrations of potentially toxic hydrocarbons in refinery effluents and in the environment should be monitored. Toward this end, relevant analyses need to be standardized and made more reliable in order to assure precision and reproducibility of results.

REFINERY OPERATIONS

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REFINERY OPERATIONS

TECHNOLOGY DESCRIPTION

World Petroleum Refining

World output of refined petroleum products in 1978 was estimated at 22.9 billion barrels (U.S. Department of Energy 1978e). Refinery production for the U.S. and the world, excluding Sino-Soviet countries for which data are unavailable, is presented in Table 1. Sino-Soviet output is estimated at 4,849 million barrels, or 21.2 percent of world output. The 5,647 million barrels produced by U.S. refineries represents 24.7 percent of the world total, or 31.3 percent of the non-Sino-Soviet world total. The world's largest refining countries, excluding the Sino-Soviet areas, were (in billion barrels) the United States (5.6), Japan (1.7), France (0.9), Italy (0.9), and West Germany (0.9).

Refinery Types and Configurations

Petroleum refineries are usually classified into general groupings based on their primary product slate or processing performed. U.S. Environmental Protection Agency (EPA) effluent regulations for petroleum refineries recognize five basic categories based on primary products and associated processing:

- o Topping--Subcategory A,
- o Cracking--Subcategory B,
- o Petrochemical--Subcategory C,
- o Lube--Subcategory D, and
- o Integrated--Subcategory E.

The topping refinery is the simplest of the basic refinery types. Topping refers to the use of simple fractionation (distillation) processes to obtain straight run fractions such as naphtha, middle distillate, and fuel oils from crude oils. Catalytic reforming, hydrotreating, and sweetening processes may be used. Since chemical cracking or cleavage processes are not directly involved, the properties of topping refinery products and pollution are directly related to the crude feedstocks used. A simplified flow diagram of a topping refinery is shown in Figure 1. The topping refinery's basic processes are essentially duplicated in the other categories of refineries.

A cracking refinery performs catalytic or thermal cracking, besides the basic topping refinery operations. Cracking significantly increases the proportion of lighter aromatics fractions.

TABLE 1
REFINERY OUTPUT VOLUME FOR 1978^a
(millions of barrels)

Product	U.S.	World
Gasoline	2,630 (46.6%)	4,813 (26.6%)
Kerosene and jet fuel	410 (7.3%)	1,353 (7.5%)
Distillate fuel oil	1,147 (20.3%)	4,073 (2.3%)
Residual fuel oil	559 (9.9%)	4,670 (25.9%)
Lubricants (including grease)	69 (1.2%)	171 (0.9%)
Refinery fuel consumption and loss)	158 (2.8%)	821 (4.6%)
Other products	<u>673 (1.2%)</u>	<u>2,134 (11.8%)</u>
Total refined products	5,647 (100%)	18,036 (100%)

^aData reflect output for the U.S. and the world, excluding the Sino-Soviet countries--the U.S.S.R., China (People's Republic), Germany (East), Poland, Hungary, Romania, Bulgaria, and Albania.

Source: Energy Information Administration 1980.

Source: Sittig 1978.

MEDIAN REFINERY FLOW SHEET

FIGURE 1
TOPPING REFINERY (SUBCATEGORY A)

Heavy and middle distillates are cracked to produce lighter hydrocarbons with a higher octane rating for blending into gasoline, kerosene, jet fuel, and fuel oils, which are in high demand. A simplified flow diagram of a cracking refinery is shown in Figure 2.

The petrochemical refinery adds petrochemical operations to those of the topping and cracking categories. Petrochemical feedstocks, such as olefins and BTX (benzene, toluene, and xylene) fractions, are included among major products for subsequent on-site petrochemical manufacture. Petrochemical processing is not considered a refinery operation in this report since it is not primarily related to energy generation or use. A simplified flow diagram of a petrochemical refinery is shown in Figure 3.

The lube refinery adds lubricating oil manufacturing processes as a major activity to those performed by topping and cracking refineries. A simplified flow diagram of a lube refinery is shown in Figure 4.

The integrated refinery includes all the major refinery operations: topping, cracking, lube oil manufacturing, and petrochemical processing. A simplified flow diagram of an integrated refinery is shown in Figure 5.

U.S. Refineries and Feedstocks

The approximately 297 U.S. refineries had a capacity of about 18 million barrels per day as of January 1980 (Aalund 1980a). Refinery processing outputs usually are expressed as barrels per calendar day (b/cd) or averaged barrels per day and as barrels per stream day (b/sd) or barrels per days in operation. U.S. refinery output by processing operation is shown in Table 2. The states with the largest total refining capacity, in decreasing order, are: Texas, California, Louisiana, Illinois, Pennsylvania, New Jersey, Indiana, Ohio, and Oklahoma. Each of these states has over 500,000 b/cd total operating capacity. Figure 6 depicts the approximate locations of most U.S. refineries.

Refinery Feedstocks

Characteristics and constituents of crude oil and residuals (heavy fractions remaining after distillation) vary greatly. Table 3 presents some of the characteristics of major feedstock crude oils and their residual fractions. Additional information showing the relative proportions of distilled fractions obtainable from feedstocks in various regions of the world is shown in Table 4.

Source: Sittig 1978.

FIGURE 2
CRACKING REFINERY (SUBCATEGORY B)

Source: Sittig 1978.

MEDIAN REFINERY FLOW SHEET

FIGURE 3
PETROCHEMICAL REFINERY (SUBCATEGORY C)

Source: Sittig 1973.

FIGURE 4
LUBE REFINERY (SUBCATEGORY D)

Source: Sittig 1978.

FIGURE 5
INTEGRATED REFINERY (SUBCATEGORY E)

TABLE 2
PROCESSING AT U.S. REFINERIES^a

Process	Production Volume (in b/sd)
Vacuum distillation	6,685,862.0
Thermal operations	1,556,425.0
Catalytic cracking	
Fresh feed	5,304,906.0
Recycled feed	817,194.0
Catalytic reforming	3,924,469.0
Catalytic hydrocracking	888,278.0
Catalytic hydrotreating	1,956,384.0
Alkylation production ^b	1,007,311.0
Aromatics/isomerization ^b	463,800.0
Lubrication oils ^b	233,252.0
Asphalt production ^b	753,699.0
Hydrogen production (mmcf/d) ^b	1,609.2
Coke production (tons/day)	48,200.0

^aCharge capacity.

^bProduction capacity.

Source: Aalund 1980a; Cantrell 1980.

FIGURE 6
DISTRIBUTION OF THE PETROLEUM REFINING INDUSTRY

TABLE 3
REPRESENTATIVE CRUDES AND THEIR RESIDUA

Crude	Arabi- an Light	Arabi- an Heavy	Kuwait	Irani- an Heavy	Su- matra Light	Vene- zuelan	Alaskan North Slope	North Sea Ninian	California
Gravity ($^{\circ}$ API)	33.3	28.1	31.3	30.8	35.3	33.3	26.3	35.1	20.9
Sulfur (wt %)	1.8	2.9	2.5	1.6	0.07	1.2	1.0	0.41	0.94
Nitrogen (wt %)	0.16	0.19	0.09	0.18	0.08	0.12	0.22	0.07	0.56
Vacuum residua (1,000 $^{\circ}$ +F)									
Gravity ($^{\circ}$ API)	8.0	4.6	7.4	6.3	20.1	10.9	7.4	13.0	5.4
Sulfur (wt %)	3.7	5.6	5.1	3.2	0.18	2.8	2.1	1.3	1.6
Nitrogen (wt %)	0.49	0.67	0.38	0.83	0.33	0.56	0.64	0.42	1.33
Asphaltenes (wt %)	11.3	20.6	12.0	14.7	7.9	16.0	8.1	6.9	12.0
Fe (ppm)		10.0	0.9	9.0	13.0	5.0	15.0	<1.0	90.0

Source: Aalund 1980b.

TABLE 4
CRUDE OIL QUALITY RANGES IN MAJOR PRODUCTION AREAS

Region	Middle East			Africa			Latin America			Western Europe			Other E. Hemisphere		
Gravity Range	Max	Av	Min	Max	Av	Min	Max	Av	Min	Max	Av	Min	Max	Av	Min
Gravity (°API)	41.0	33.2	19.0	45.0	36.3	24.0	34.0	27.8	17.0	44.0	36.7	35.0	44.0	34.8	29.0
Sulfur (wt %)	1.3	1.6	4.6	0.1	0.2	0.5	0.2	1.4	2.4	0.2	0.3	1.0	0.1	0.1	0.1
Yields (vol %)															
Gasoline	23.0	22.0	8.0	30.0	26.0	14.0	14.0	16.0	7.0	33.0	26.0	22.0	43.0	22.0	7.0
Middle distillate	38.0	33.0	28.0	39.0	37.0	24.0	56.0	30.0	24.0	34.0	36.0	37.0	46.0	42.0	21.0
Residue	35.0	43.0	64.0	27.0	34.0	61.0	29.0	53.0	68.0	28.0	35.0	38.0	8.0	35.0	71.0

Source: Cuddington 1980.

Sulfur in Crude Oil Feedstocks

The removal of sulfur from crude oil during the production of refinery products is a major task performed by refining processes. Combustion of sulfur-containing petroleum products leads to the formation of sulfur dioxide (SO_2), an objectionable pollutant. Table 5 presents data concerning sweet (low sulfur) and sour (high sulfur) crude oils and other feedstocks used by U.S. refineries. The type of feedstocks a refinery can process depends largely on the types and configuration of processing equipment it employs. Sulfur compound removal is primarily performed by sweetening and hydrotreating processes. Many U.S. refineries, especially older and smaller refineries, can only handle crude oil feedstocks with a limited aggregate sulfur content. Many of these refineries must use imported sweet (low sulfur) in crude oil as their major or supplemental feedstock.

Sulfur in crude oil occurs as malodorous hydrogen sulfide (H_2S) and as thiols (mercaptans), thiophenes, sulfides, and polysulfides. The nature and concentration of sulfur compounds varies with each crude oil. Sulfur compounds are removed by general refining processes, but, in general, sulfur compounds tend to remain distributed in crude oil fractions and in their final products in proportions that increase with increasing molecular weight and boiling point.

Sulfur content, usually expressed in terms of percent by weight of sulfur, may not appear high. However, the percentage of sulfur-containing molecules can be very high, perhaps exceeding half the total crude oil constituents. The sulfur may be incorporated in large molecules comprising crude oil. This sulfur may be removed by catalytic hydrogenation processes such as hydrotreating (hydrodesulfurization). These processes release the sulfur as gaseous hydrogen sulfide and, to a lesser extent, volatile thiols. Resultant potentially toxic and malodorous process streams are usually processed to reclaim elemental sulfur. Crude oil and fractions are often washed with caustic solutions or further fractionated to remove these sulfur compounds from the liquid phase. The proportion, complexity, and stability of sulfur compounds are higher in heavier residual crude oil fractions. More intense pressures, temperatures, and high purity hydrogen are required to yield low sulfur residual fuel oils. Low sulfur fuels for power generation and industrial use (as required by Federal regulations) are produced by these energy-intensive methods.

Refinery Process Stream Nomenclature

Petroleum refinery process streams are complex mixtures for which precise definitions and chemical constitution-based nomenclature are lacking. The composition of process streams may vary

TABLE 5
REFINERY FEEDSTOCKS
(1980 estimates)

Type of Feedstock	Input (barrels/day)	Crude and Field Condensate (percent)
Sweet crude oil (less than 0.5% weight sulfur)	8,004,000	50.5
Medium light crude oil (0.5-1.0% weight sulfur)	2,210,000	14.0
High sulfur crude oil (greater than 1% weight sulfur)	<u>5,513,000</u>	<u>34.8</u>
Total crude oil	15,747,000	99.3
Field condensate	115,000	0.7
Other feedstocks	<u>1,320,000</u>	<u>--</u>
Total refinery input	17,182,000	100.0

-- Represents zero or rounds to zero.

Source: Aalund 1980b.

greatly depending on a multitude of factors, including the crude oil source, process conditions and sequence, and chemicals used.

To aid development of the Toxic Substances Control Act (TSCA) Inventory, EPA issued an addendum to the Candidate List of Chemical Substances concerning the nomenclature to be used for reporting petroleum refinery intermediates and products (U.S. Environmental Protection Agency 1978). Refinery process streams are generically defined according to their source (process), general hydrocarbon composition, predominant carbon numbers and hydrocarbon types, and boiling range or other physical characteristics. Refinery by-products, waste products, proprietary names, impurities, and additives are not included in this publication. Chemical Abstracts Service (CAS) Registry Numbers are associated with all process streams. The adequacy of these definitions, their acceptance and use by refiners, and the degree to which process streams are considered proprietary information by many refiners will be evident after the initial TSCA Inventory is published.

Petroleum Refining Processes and Technology

The following are descriptions of major refinery processes. Information was obtained from several sources (Sittig 1978; Gulf Publishing Company 1978; U.S. Environmental Protection Agency 1974; and Dickerman et al. 1977).

Crude Desalting

- o Application: Inorganic salts, water, suspended solids, and certain water soluble compounds must be removed from crude oils to prevent equipment fouling, corrosion, and catalyst poisoning in downstream processing units.
- o Input materials: Crude oil; oil bearing water.
- o Products: Desalted crude oils for fractionation processing.
- o Process description: Crude desalting is essentially a solvent extraction process using water as the extracting medium. In chemical desalting, chemical deemulsifiers (surfactants) are added to the crude oil, water is added, and the resulting emulsion is heated to 150 to 350°F and held in a settling tank. Salts and other impurities dissolve in or attach to the water globules which settle out and coagulate.

Electrical desalting differs from chemical desalting; electrical differentials are applied and deemulsifiers are used only for crude oils with a high suspended solids content. Suspended water globules

are concentrated in the bottom portion of the settling tank under the influence of a high voltage electrostatic field.

In both types of processing, desalted crude is continuously drawn off the top of the settling tank and the wastewaters are continuously drawn off the bottom. Ammonia may be added to reduce corrosion.

- o Operating parameters: Temperature, 150 to 350°F (66 to 177°C); and pressure, 2.8+ kg per cm² (40+psi).
- o Wastes: Approximately 1.5 to 2.5 gallons of wastewater per barrel of crude (35 to 60 liters per m³) is discharged to the wastewater treatment or sewer system. Water discharge contains extracted chlorides, sulfides, bicarbonates, free oil, ammonia, phenol, and suspended solids. This wastewater has a relatively high biological oxygen demand (BOD) and chemical oxygen demand (COD), and contains chlorides and other dissolved materials that may cause adverse effects if discharged untreated into water bodies.
- o Trends: Electrical desalting is replacing chemical desalting. Two-stage electrical desalting and supplemental chemical desalting may be used as dirtier crude oils are processed in refineries.

Crude Oil Fractionation

- o Applications: Crude oil is distilled using single or multiple fractionating columns and processes to separate it into intermediate product streams.
- o Input materials: Crude oil (desalted).
- o Products: Crude oil fractions differentiated by boiling point ranges.
- o Process description: Many combinations of equipment configurations and distillation products are encountered, depending on the crude oil used and the desired product mix. Usually, crude oil is preheated using recovered process heat, charged to a direct-fired furnace, and charged to an atmospheric fractionation (distillation) column at about 650 to 700°F (344 to 371°C).

The vaporized oil condenses in the vertical fractionation column, with lighter (higher boiling point) fractions diffusing and condensing toward the top of the column and heavier (lower boiling

point) fractions condensing or remaining at the bottom. Fractions are continuously drawn off and diverted for further processing or distribution.

Residual, high boiling point materials are usually withdrawn into a vacuum fractionation column for separation into lubricants, residual oil fractions, and/or catalytic cracking feedstocks. Heavy asphalt residual base stock is withdrawn from the bottom of the column. Light fractions may be further fractionated and degassed to produce straight-run gasoline. Gases removed during fractionation include ethane, methane, propane, and butane.

Steam distillation may be used for stripping (extracting) sulfur-containing compounds.

- o Operating parameters: Process takes place at atmospheric pressure or in a partial vacuum; temperature is approximately 248°F (120°C) at the top of the fractionation column and 698°F (370°C) at the bottom. Typical installations are energy-intensive, requiring about 100,000 Btu's per barrel of crude oil for process heat, 17 kg of steam per barrel (143 kg per m³) of crude oil for stripping, and 82 liters of cooling water per bbl (690 liters per m³) of crude oil.
- o Wastes: Condensed water-containing sulfides occur in high concentrations when sour (high sulfur) crudes are processed. They are usually discharged to the wastewater treatment or sewer system. The wastewater also contains ammonia, phenols, oil, chlorides, thiols (mercaptans), and other water-soluble compounds. Barometric condensers that use water jets to reduce pressure for vacuum distillation may contribute to the formulation of oil emulsions. However, the use of surface condensers in which oil does not come into contact with water does not lead to this waste. Fraction sampling may produce some wastes.

Distillation is essentially a closed process, in terms of atmospheric releases. Fugitive hydrocarbon emissions and process heaters are the major sources of atmospheric emissions.

- o Trends: Larger and more complex fractionation systems reflect the general industry trend toward larger, more complex, refineries. Multiple atmospheric and vacuum distillation unit configurations with increased sidestreams and products represent another trend. Surface condensers for vacuum distillation are replacing barometric condensers.

Drying and Sweetening

- o Application: Sweetening processes remove sulfur compounds, primarily hydrogen sulfide, thiols (mercaptans), and thiophenes, to improve odor, color, and oxidation stability; to lower fuel sulfur content to comply with environmental regulations; and to lower the amount of tetraethyl lead required to boost gasoline octane ratings. Drying removes water and both processes lower concentrations of carbon dioxide and other impurities.
- o Input materials: A wide variety of intermediate and final products are dried and sweetened. Usually middle distillate liquids, such as gasoline, kerosene, jet fuels, home heating oils, and sometimes sour gases, are processed.
- o Process description: Most sweetening processes involve the use of a caustic (basic) regenerable sorbent liquid, usually diethanolamine, to extract sulfur compounds. Washing solutions are regenerated by heating and air or steam stripping. Electrical fields may be applied to facilitate separation. Drying is performed using sand filters, absorptive clay beds, or other water adsorptive or absorptive media.

Chemical sweetening processing involves three major activities: (1) oxidation of thiols (mercaptans) to less objectionable disulfides; (2) removal of thiols; and (3) destruction or removal of other sulfur compounds including hydrogen sulfide and elemental sulfur (also performed through hydrotreating). Processes that convert thiols into disulfides include Doctor Sweetening, copper sweetening, Bender, and Merox.

Inhibitor sweetening uses a caustic solution and a substituted phenylenediamine substance to catalytically oxidize thiols to disulfides in gasoline and related products. The phenylenediamine substance acts as an inhibitor, reducing the amounts of oxidation inhibitors normally added later to final gasoline blends.

- o Operating parameters: Dependent on process(es) used.
- o Wastes: Spent caustic solutions are the most common wastes from drying and sweetening. Spent caustics may be characterized as sulfidic or phenolic, depending on the oil treated. Spent sulfidic caustics contain high sulfide concentrations. Spent phenolic caustics contain high concentrations of phenol, cresols, xylenols, and sulfur compounds. Spent caustics have very high BOD and COD. When diethanolamine is used, a

small amount--about one gallon per 100 barrels (four liters per 159 m³)--of waste must continually be replaced.

Water washing of treated products and regeneration of treating agents, such as sodium plumbite (Na_2PbO_2) used in Doctor Sweetening and copper chloride, may cause small amounts of these substances to be discharged in aqueous waste streams.

Sweetening of sour gases results in an H_2S -rich gas stream that may be flared, burned as fuel, or processed to recover elemental sulfur.

No atmospheric emissions, other than fugitive emissions, are associated with these processes.

- o Trends: Air pollution standards to control sulfur emissions have resulted in a strong trend toward replacing sweetening processes with hydrotreating, because hydrotreating removes almost all, not just select, sulfur compounds. Sweetening will continue to be used because it is effective and economical. Sweetening processes producing toxic or high waste loads, such as Doctor Sweetening, will tend to be replaced by lower waste-producing processes.

Solvent Refining and Dewaxing

- o Applications: Solvent refining includes a multitude of processes that extract desired and undesired components from feedstocks on the basis of differential solubilities. Most frequently, the processes are used to separate aromatic from non-aromatic components, dewax lubrication oils, deoil waxes, and to remove undesired unstable, acidic, sulfur, organometallic, naphthenic, and/or nitrogen compounds. Removal of aromatics improves diesel fuel combustion and increases gasoline octane ratings.
- o Input materials: A wide variety of feedstocks are used, including fractionated crude oils, deasphalted oil, naphtha, and catalytic reforming products. Feedstocks vary with the processes and desired products.
- o Process description: Hydrocarbons and other substances are separated on the basis of their relative solubilities in different solvents. Solvents used in the various processes include acetone, benzene, dichloroethane, diglycolamine, formylmorpholine, furfural, methyl-ethylketone, methyl-isobutylketone, n-methylpyrrolidone, methylene chloride, pentane,

phenol, propane, propylene, sulfolane, sulfur dioxide, sulfuric acid, tetraethylene glycol, toluene, urea, and water.

Processing usually involves:

- (1) Drying and/or deaeration of the feedstock;
 - (2) Using countercurrent solvent extraction techniques;
 - (3) Separation of the bulk of the solvent from the product by heating and fractionation or evaporation;
 - (4) Removal of solvent traces from the product by steam stripping or vacuum flashing (exposure to high vacuum); and
 - (5) Solvent purification for reuse.
- o Products: refined oils, fuels, and waxes; high octane blending components; and high-purity aromatics.
 - o Operating parameters: Solvent extraction processes may involve heating or refrigeration of feedstocks and/or products. Electrostatic precipitation may be used to separate inorganic compounds.
 - o Wastes: The solvents themselves are the major potential pollutants from solvent refining. Many of the solvents such as phenol, glycols, and amines have high BOD. Solvents are nearly always recycled, but leaks and spills may occur. Water from the bottom of fractionation towers containing oil and solvent is the main aqueous waste stream.
 - o Trends: Solvent refining will increase as quality requirements for refinery products increase and as demand for extracted aromatics for petrochemical production increases.

Hydrotreating

- o Applications: Like hydrocracking, hydrotreating involves the catalytic combination of hydrogen with feedstock hydrocarbons. However, in hydrotreating, the degree of saturation is not as severe. Hydrotreated feedstocks may be used as blending stocks for final products, or they may be used as feedstocks for additional processing, especially catalytic reforming which requires hydrotreating as pretreatment to maintain catalyst viability and to yield a better product.

Hydrotreating causes sulfur-bearing compounds to form hydrogen sulfide and nitrogen-bearing compounds to form ammonia. Approximately 90 percent of the sulfur and nitrogen are removed from the feedstock. Catalyst regeneration associated with subsequent catalytic cracking will release less sulfur dioxide to the atmosphere.

- o Input materials: Many processes using practically all possible feedstocks are employed. Naphthas, including gasolines, account for the largest share of hydrotreated feedstocks.
- o Process description: Catalysts and feedstocks used account for the major differences among the available processes. In most processes, the feedstock is mixed with hydrogen, heated, and charged under pressure to catalytic reactor units. Reactor products are cooled, hydrogen separated and recycled, and desired and undesired fractions separated. The degree of hydrogenation increases with pressure, temperature, and contact time. Excessive contact time and temperature lead to coke formation. Most hydrotreating processes require constant hydrogen input from a hydrogen generation unit.
- o Products: Feedstocks with low sulfur, nitrogen, and olefin contents, and improved stability.
- o Operating parameters: Pressures at 100 to 3,000 psig, depending on the process; temperatures at 350 to 850°F (176 to 454°C), depending on the process, but usually at 600 to 800°F (315 to 426°C); and hydrogen consumption, usually at less than 200 scf per barrel of charge.
- o Wastes: The concentration and quantity of wastes depend on the process used. Wastewater streams come from steam strippers, sour water stripper bottoms, and accumulators on fractionation columns. Sulfides and ammonia are the major pollutants. Phenols may be present if a high boiling point feed is used.
- o Trends: Hydrotreating has primarily been used to treat light materials, such as naphthas and gasolines; but with continued developments heavier fractions are being processed. Hydrotreating is increasing, because it can be applied to most feedstocks, is flexible, and reduces gross air and water pollution. Hydrotreating and hydrocracking units are being installed at faster rates than other refining process units.

Hydrocracking

- o Applications: Hydrocracking is probably one of the most economically important processes in modern U.S. refineries.

Heavy sour feedstocks may be converted into sweeter, lighter, more profitable products, especially gasoline, other light fuels, and petrochemical feedstocks.

Hydrocracking combines catalytic cracking of hydrocarbons with catalytic hydrogenation under high pressures. Cracked hydrocarbons are hydrogenated to yield totally saturated products with lower aromatic contents.

Sulfur and nitrogen compounds are usually removed in the process. Most hydrocracked fractions do not require additional sweetening.

- o Input materials: A wide range of feedstocks, including most distillate fractions, gas oils, heavy sour crude oils, and residuals, may be hydrocracked. Hydrocracked fractions may be further processed. Precious metal compounds may be employed as catalysts.
- o Process description: The process is much like hydrotreating, but takes place in a hydrogen atmosphere at higher pressures and lower temperatures. Reactor outputs are separated, and fractionated; hydrogen is recycled to the reactor, and heavier-than-desired fractions are recycled to the reactor. Olefins (alkenes) formed during cracking are saturated with hydrogen.
- o Products: Gasoline, high octane isoparaffins, jet fuels, diesel fuels, and low-sulfur fuel oil.
- o Operating parameters: Temperature at 780 to 1,500°F (400 to 800°C), pressure at 100 to 2,000 psig.
- o Wastes: Aside from the process heaters, atmospheric emissions result from catalyst regeneration operations and fugitive hydrocarbon emissions. Large quantities of carbon monoxide may be released from catalyst regeneration.

A sour water and ammonia-containing waste stream forms from steam condensation during catalyst steam stripping and regeneration.

Catalysts usually have a life of about 2 years, after which they may be reclaimed or disposed of as solid waste.

- o Trends: Hydrocracking capacity is growing because it allows for adjusting refinery intermediates and products to meet market demands. More profitable products such as high-octane

unleaded gasoline may be produced than can be obtained through other processes.

Alkylation

- o Applications: Alkylation is used to convert normally gaseous hydrocarbons to high-octane gasoline components. Isoparaffins (secondary alkanes), usually isobutane, are catalytically combined (condensed) with olefins (alkenes), such as propylene, butylene, and pentylene, using a strong acid catalyst to form longer chain hydrocarbons. When butylene undergoes alkylation with isobutane, the major product is isooctane (2,4,4-trimethylpentane), the reference material for octane ratings having an octane number of 100.
- o Input materials: The process uses petroleum gases (e.g., isoparaffins, usually isobutane; and olefins, usually propylene, butylenes, and pentylenes).
- o Process description: A dry, olefinic gaseous feedstock is mixed with excess isobutane and reacted with an acid catalyst in a reaction vessel. The catalysts may be hydrofluoric acid (HF), aluminum chloride (AlCl_3), or sulfuric acid (H_2SO_4). Reactor output is separated, the acid phase recycled to the reactor, and hydrocarbons are passed through a caustic and water wash and fractionated. Excess isobutane is recycled to the reactor and by-products (normal butane and propane) are removed.

When sulfuric acid is used as the catalyst, acid and organically combined sulfur are removed by caustic scrubbing prior to fractionation. The reactor temperature may be maintained through refrigeration.

- o Operating parameters: Temperature at about 120°F (48°C) for AlCl_3 , about 50 to 61°F (10 to 16°C) for H_2SO_4 , and about 81 to 90°F (27 to 32°C) for HF; pressure at 100 to 150 psig (7 to 10 kg per cm^2) reported for HF and H_2SO_4 .
- o Wastes: Catalytic alkylation processes are generally closed systems with no process vents to the atmosphere, except for those from fired heaters. HF units are generally closed systems. However, any leaks or spills involving fluorides are hazardous health and safety problems. Alkaline (caustic) scrubbers remove any fluorides that could be incidentally discharged in process streams. HF acid regeneration units

usually produce a sludge material that is either incinerated or alkaline washed to produce solid waste fluorides. Fluorides removed from the output are also disposed of as solid wastes.

Wastewaters from sulfuric acid process product scrubbing are usually processed by the refinery's water neutralization and wastewater treatment systems to recover the acid or to neutralize other wastes. Waste streams from scrubbing usually contain sulfides, suspended and dissolved solids, oils, and other contaminants.

- o Trends: Alkylation capacity may be expected to increase to satisfy demands for high-octane gasoline. However, feedstock olefins may be routed to make more profitable petrochemicals. Alkylation is replacing polymerization as the means of converting olefins to gasoline because its products have higher octane ratings.

Isomerization

- o Applications: Isomerization is used to convert normal C_4 to C_6 primary alkanes (butane, pentane, and hexane) into their respective isoparaffins (secondary alkanes). Isobutane formed may be used as a feedstock for alkylation processes. Isopentane and isohexane have sufficiently high octane ratings to be used directly as blending components for gasoline.
- o Input materials: Normal butane, pentane, and hexane-containing fractions from a number of process streams.
- o Process description: Sweet, dry feedstock is mixed with hydrogen and organic chlorides as a promoter; then it is heated, and passed over a catalyst. The use of chlorinated platinum-aluminum oxide catalysts has been reported. Hydrogen is separated from the product and recycled. Liquids are fractionated to separate normal paraffins from isoparaffins and isoparaffin product streams are neutralized with alkaline materials. Normal paraffins are recycled, isobutane is sent on to alkylation units, and isopentane and isohexane are used for gasoline blending. Hydrogen is used in the process to hydrogenate side-reaction unsaturated compounds and to prevent polymerization.
- o Operating parameters: Temperature at 464 to 491°F (240 to 255°C), and pressure at 300 to 400 psig (21 to 28 kg per cm^2).

- o Wastes: Isomerization is essentially a closed process. The neutralization step produces some aqueous wastes that would probably be relatively low in sulfide, ammonia, phenolics, and BOD.

Catalysts are generally replaced after 2 years and reprocessed for platinum and precious metal recovery at plants that are separate from the refinery.

Catalytic Reforming

- o Applications: Reforming is primarily used to increase the octane rating or antiknock qualities of naphtha-rich fractions used as gasoline blending stock. Although a number of reactions take place, the predominant reactions are the dehydrogenation and aromatization of naphthenes (cyclic alkenes) to form stable C6 to C8 aromatics, such as benzene, toluene, xylenes, and others. These aromatics have a higher Research Octane Number (RON) than their precursors and are usually used for gasoline blending. Catalytic reforming also causes other reactions to occur: paraffin hydrocracking, paraffin dehydrocyclization, and paraffin isomerization. Hydrogen from dehydrogenation reactions is a major by-product of catalytic reforming. Some hydrogen may be recycled to sustain reactor pressure and to suppress coke formation caused by polymerization. Most of the hydrogen is used for other processes, such as hydrocracking, hydrotreating, isomerization, and petrochemical processing.

Bi-metallic and multi-metallic catalysts containing platinum and other metal promoters, such as rhenium, are used in most processes.

- o Input materials: Feedstocks are desulfurized (sweetened) naphthas and naphthene-rich fractions. Usually the feedstock has been hydrocracked. Removal of sulfur, nitrogen, arsenic, and other metals from feedstock is required to prevent catalyst poisoning (deactivation).
- o Process description: Platforming is the most widely used catalytic reforming process. The charge and recycled gases are heated and passed through a series of catalytic reactors. Reactor output is separated into liquid and gas streams, the gases are compressed for recycling, and liquids are stabilized to the desired vapor pressure. Catalysts may be continuously withdrawn, regenerated, and returned to the top of the reactor units. Alternatively, the catalyst may be

periodically regenerated by taking the reforming units off stream, or one reactor may be regenerated at a time.

- o Products: High-octane gasoline fractions; benzene, toluene, xylenes, and other aromatics; and isobutane. Hydrogen is a significant by-product.
- o Operating parameters: Temperature varies with installation, feedstock, and desired products. Pressure is the most important parameter and controls the relative amounts of dehydrogenation and hydrocracking reactions.
- o Wastes: This is essentially a closed system process. Slight atmospheric emissions may occur from catalyst regeneration, mostly as carbon monoxide.
- o Trends: Catalytic reforming processing has increased to supply increased amounts of high-octane gasoline.

Thermal Cracking

- o Application: Thermal cracking involves the breaking down of heavy oil fractions, usually residuals from vacuum fractionation processes, into lighter (lower-molecular-weight) middle distillate and heavy fuel oil fractions. Heat and pressure are used, rather than catalysts. Heat breaks the bonds within hydrocarbon chains and, to a lesser extent, may cause recombination (polymerization) to form larger molecules. Coking processes yield coke, which is widely used as a fuel in industry.
- o Input materials: Residual crude oil fractions, asphalts, and unfractionated crude oils.
- o Process description: Visbreaking is a mild form of thermal cracking that causes little reduction in boiling point range, but significantly lowers the viscosity of the feed. The feed is heated in the visbreaking heater, vapors are removed, and the heavier fractions are recycled. The output may be fractionated for gasoline, fuel oils, gas oil, and gases.

Coking is a severe form of thermal cracking, often using a residual feedstock that has resisted other cracking processes. Feed is heated and held at a high temperature. The vapor phase undergoes further cracking, and the liquid phase undergoes successive cracking and polymerization to form vapors and coke. Vapor phases are fed into fractionation units. Coking units usually have at least two drums--one

in service while the coke from the other is removed with high-pressure water jets.

- o Products: Coke, fuel oils, gas oil, naphtha, gasoline, and gases.
- o Operating parameters: Coking heater outlet temperatures are about 900 to 950°F (482 to 510°C), and pressures are about 20 to 60 psig (1.4 to 4.2 kg per cm²). In general, an increase in temperature increases light hydrocarbon yields and decreases coke production, while higher pressures have the opposite effect.

Visbreaking units use steam at about 575°F (302°C) and 300 psig (21 kg per cm²).

- o Wastes: Water, usually containing various oil fractions and high in BOD, COD, ammonia, phenol, and sulfides, results from thermal cracking fractionation units. Wastewater may be highly alkaline.
- o Trends: Visbreaking and coking are the two major forms of thermal cracking in the U.S. Older thermal cracking processes have been practically eliminated.

Catalytic Cracking

- o Applications: Catalytic cracking is used to increase the yield and quantity of gasoline and other desirable lighter products, while minimizing the yield of residual or heavier products.
- o Input materials: A wide variety of feedstocks are used, including naphthas, gas oils, coke distillates, deasphaltized oils, and sometimes unfractionated crude oils.
- o Process description: Catalytic cracking involves the use of at least four chemical reactions--thermal decomposition, primary catalytic reactions at the catalyst surface, secondary catalytic reactions between the primary products, and polymerization and removal of products from reactions by absorption on catalyst surfaces as coke.

Catalysts include synthetic and natural silica-alumina, treated bentonite clay, fuller's earth, aluminum hydrosilicates, zeolites, and bauxite. Catalyst forms include beads, pellets, and powders, and they are used in fixed, moving, or fluidized beds. Fluidized-bed catalytic cracking (FCC) uses

finely powdered catalysts that, when mixed with a gas, have physical properties similar to liquids. This fluid catalytic cracking accounts for most of the catalytic cracking capacity in the U.S.

In fluid catalytic cracking, hot powdered catalyst is lifted by the incoming feed which vaporizes upon contact. Reactor vapors pass through cyclone separators that separate powdered catalyst from gaseous reaction products. Vapors enter a fractionation column where desired products are removed and heavier fractions are usually recycled to the reactor. Spent catalyst passes to a steam stripper to remove residual hydrocarbons, and then to a regenerator where coke deposited on the catalyst is burned off through combustion with preheated air. The degree of combustion, by design, may vary from complete combustion, to CO_2 or any CO_2 -to- CO ratio. The hot regenerated catalyst is fed back to the reactor.

Flue gases from catalyst regeneration pass through cyclone separators and/or electrostatic precipitators to remove catalyst. Flue gases containing appreciable quantities of CO may be burned in a CO boiler. The energy content of pressure, flue gas heat, and heat from CO combustion are frequently recovered to drive equipment or generate steam.

Fixed-bed catalytic cracking employs stationary catalyst beds. Moving-bed catalytic processing uses catalyst beads which fall through the reaction chambers.

- o Products: Gases (alkanes), gasoline, middle distillates, and petrochemical feedstocks.
- o Operating parameters: Fluidized-bed catalytic cracking reactor temperatures are 887 to 1,022°F (475 to 550°C), and pressures are 10 to 30 psig (0.7 to 2.1 kg per cm^2). With catalyst regenerators, the temperatures are 1,247 to 1,400°F (675 to 760°C), and pressures are 15 to 35 psig (1 to 2.5 kg per cm^2). Moving- and fixed-bed units operate under similar conditions.
- o Wastes: Catalytic cracking is a major source of refinery pollution. Catalyst regeneration, involving steam stripping and decoking, results in fluid waste streams containing oil, sulfides, phenols, ammonia, and other substances. The catalyst steam stripper has been reported to use five gallons of water per barrel of feed (120 liters per m^3), which is routed to wastewater treatment systems. Atmospheric emissions from generators with no emission controls include:

- (1) Particulates--32 to 116 gr per bbl (0.267 to 0.976 kg per m³) fresh feed;
- (2) Sulfur oxides--107 to 185 gr per bbl (0.898 to 1.505 kg per m³) fresh feed;
- (3) Carbon monoxide--4,677 gr per bbl (39.2 kg per m³) fresh feed;
- (4) Hydrocarbons--75 gr per bbl (0.630 kg per m³) fresh feed;
- (5) Nitrogen oxides--13 to 50 gr per bbl (0.107 to 0.416 kg per m³) fresh feed;
- (6) Aldehydes--6.44 gr per bbl (0.054 kg per m³) fresh feed; and
- (7) Ammonia--18 gr per bbl (0.155 kg per m³) fresh feed.

Atmospheric emissions controlled by CO boilers yield negligible amounts of carbon monoxide, a quantity of particulates ranging from 4.3 to 21 gr per barrel (0.036 to 0.175 kg per m³) of fresh feed, and somewhat lesser amounts of other emissions. The CO boiler has too low a temperature (about 700°C) to consume the other combustible emissions.

Aqueous wastes, primarily condensed steam from catalyst stripping, contain hydrogen sulfide, mercaptans, ammonia, and phenols. These wastewaters are alkaline and have high COD and BOD. Sulfide and phenols concentrations may vary greatly, depending on the feedstock fractions or crude oils.

- o Trends: Industry is turning increasingly to catalytic cracking and larger sized units because of the demand for high-octane gasolines and petrochemical feed stocks. Fluid catalytic cracking is more competitive than fixed- or moving-bed catalytic cracking. However, many existing units may be expected to remain in operation for several years.

Polymerization

- o Applications: Polymerization is used to convert olefin (alkene) feedstocks into higher-octane gasoline blends. Polymerization is much like catalytic alkylation. However, two olefins are combined, rather than an olefin and an iso-paraffin, as in alkylation. Polymerization is decreasing

in use because olefins yield a higher return when used as feedstocks for petrochemicals.

- o Input materials: Any combination of olefins, such as ethylene, propylene, butylene, and/or pentylene.
- o Process description: Olefin gases are passed over catalysts where polymerization occurs. Phosphoric acid catalyst is usually used, but sulfuric acid is used in some older units. The reaction is exothermic, requiring the use of cooling water and injection of cold feed into the reactor. Vapor products are fractionated, acid catalysts are recycled, and acid in products is removed by caustic washing.
- o Operating parameters: Temperature at 300 to 435°F (149 to 223°C), and pressure at 150 to 1,200 psig (10.5 to 84 kg per cm²).
- o Wastes: Polymerization is a closed process with no purposeful atmospheric emissions. Alkaline solutions from caustic washing and acids washed out during maintenance are liquid wastes. Acid catalysts adhering to solids yield solid waste when periodically removed.
- o Trends: Polymerization does not increase octane ratings as much as alkylation and required olefin feedstocks may be more profitably used in petrochemical processing. The polymerization capacity has been decreasing in U.S. refineries.

Deasphalting

- o Applications: Deasphalting, or the removal of asphalt residues, is used to upgrade several intermediates and products. Deasphalting improves lubricating oil qualities and deasphaltized oils are among preferred feedstocks for catalytic cracking and hydrocracking processes. Extracted asphalt may be utilized by blending with other products or the asphalt output may be marketed. Deasphalting removes some sulfur and nitrogen compounds, metals, carbon residues, and paraffins from the feedstock.
- o Input materials: The feedstock is usually a vacuum fractionation or other residual oil. Lubricating oils and asphalts may be processed.
- o Process description: Deasphalting is usually performed by solvent extraction using propane or other light hydrocarbons. Resulting deasphaltized oil and asphalt phases are processed

through evaporation and steam stripping to separate and recover propane, oil, and asphalt products. Oil and asphalt products may be further vacuum or atmospheric fractionated.

- o Products: Asphalt or heavy fuel blending stocks and deasphalted oils.
- o Operating parameters: Temperature at 160 to 220°F (70 to 105°C), pressure at 450 to 600 psig (32 to 43 kg per cm²), and steam at 30 to 140 lbs per bbl (86 to 400 kg per m³) of feed. Typical units have operating capacities of 2,700 to 4,400 bbls per day (17,000 to 28,000 m³ per day).

About 300 gallons of feed per bbl (7,250 liters per m³) of cooling water are required.

- o Wastes: Atmospheric emissions are process heater flue gases and fugitive emissions from high-pressure equipment. Condensed steam contaminated with hydrocarbons is usually routed to the refinery wastewater treatment facility.
- o Trends: Deasphalting may be expected to increase as product quality requirements become more stringent, as demand for lubrication oil increases, as crude oil supplies become heavier, and as demand for petrochemical feedstocks increases. Solvent refining feedstocks often require deasphalting and the future of deasphalting is thus linked to that of solvent refining.

Asphalt Blowing

- o Applications: Asphalt blowing oxidizes asphalt hydrocarbons, increasing their melting temperature, hardness, and weathering properties.
- o Input materials: Vacuum fractionation residue and asphalt from deasphalting units.
- o Process description: Asphalt is batch heated and air is blown through it. Exothermic oxidation reactions proceed without additional heat input. Blowing is stopped when the desired product specifications have been attained. Reaction conditions foster the development of polycyclic aromatic hydrocarbons (PAHs), many of which are carcinogenic.
- o Operating parameters: Temperature at 436°F (260°C) initiates oxidation reactions.

- o Products: Partially oxidized asphalt (bitumen).
- o Wastes: Oxidizer overhead gases, rich in hydrocarbon vapors from blowing operations, are usually incinerated. Vented gases constitute one of the more objectionable forms of air pollution from a refinery. They have highly objectionable odors and contain a large proportion of polycyclic aromatic hydrocarbons.

Grease Manufacture

- o Applications: Grease primarily consists of mixtures of soaps and lubrication oils. Sodium, calcium, aluminum, lithium, and barium soap bases are produced by saponification of fatty acids and oils. The properties of a grease are largely determined by its soap component. Soaps are manufactured at the refinery or purchased as raw materials.
- o Input materials: Alkali earth metal hydroxides and fatty acids for soap manufacture and lubricating oils, waxes, and other materials for mixture with the soaps.
- o Process description: Soaps are manufactured by saponification--through the heating and mixing of fatty acids and alkali earth hydroxides. Lubricating oils, waxes, and additives are mixed with the soap base in a heated kettle and the resulting grease may be further processed to final specifications.
- o Products: Lubricating greases.
- o Operating parameters: Temperatures at 400° to 600°F (204° to 316°C) are reported for heating cycles.
- o Wastes: Aqueous effluent results when process units are washed and soaps and oil are discharged to a sewer or wastewater treatment system.
- o Trends: Increased use of sealed grease fittings in newer automobiles may lead to a decrease in grease manufacture.

Wax Manufacture

- o Applications: Paraffin and microcrystalline waxes with low oil content, high melting point, and other desired properties are manufactured.

- o Input materials: High oil content waxes from crude fractionation and/or waxes from dewaxing of lubricating oils are the feedstocks. Feedstock or product material may be hydro-treated.
- o Process description: In the most common method of wax finishing, the feedstock is dissolved in a solvent and chilled in double-pipe, scraped-surface chilling equipment to a temperature required to crystallize only the deoiled wax components having the desired melting point. Wax crystals are vacuum filtered and oils in the wax cake are washed out with cold solvent. The resulting wax cake is removed and refiltered; then filtrates are recycled.
- o Products: Paraffin and micro-crystalline waxes with oil contents below 0.5 percent.
- o Wastes: Wax manufacture is not a significant source of wastes. Solvents and oil may enter wastewater systems through leakage. Wax in sewer systems may interfere with settling operations in wastewater treatment plants and may clog sewers.

Hydrogen Manufacture

- o Application: Several refinery processes, such as hydrotreating, hydrocracking, and associated petrochemical processes, require hydrogen feedstocks. Hydrogen by-products from catalytic reforming frequently do not satisfy a refinery's need for hydrogen.
- o Input materials: Usually gases, such as natural gas, refinery gases, propane, and butane. In addition, heavy fuel oil can be used in the partial oxidation process.
- o Process description: Steam reforming, the most widely used process, involves the mixing of sweetened gases with superheated steam and the charging of the mixture to a hydrogen furnace consisting of a vertical combustion chamber with suspended alloy tubes containing a nickel-based catalyst. Hydrocarbons are catalyzed to hydrogen, carbon dioxide, and carbon monoxide. Gases are cooled by addition of steam and condensate and passed through a converter unit which reacts (oxidizes) carbon monoxide with water to produce additional carbon dioxide and hydrogen. Gases from the converter are cooled and passed to a carbon dioxide removing unit. Here, CO₂ is absorbed in amine solutions. These solutions are

reactivated by heating and the CO₂ is vented to the atmosphere.

- o Operating parameters: Superheated steam (steam at high temperature and pressure) is employed in the combustion chamber.
- o Products: Hydrogen, typically 98 percent hydrogen with traces of CO₂ and CO.
- o Wastes: Few wastes occur from hydrogen manufacture. Free carbon removed from a water wash associated with the partial oxidation process may be a minor waste.
- o Trends: Hydrogen production at refineries may be expected to increase to satisfy hydrogen demands for hydrotreating, hydrocracking, and petrochemical processing.

Process Heaters and Steam Production

- o Applications: Process heaters are used throughout the refinery to heat feedstocks to reaction temperatures and for distillation. Steam is produced in one or more units for direct use in various processes, for heating, and to drive equipment. Steam generation units may be used to recover waste heat and for cooling.
- o Input materials: Refinery gases and residual and distillate fuel oils are used as fuels. Some fuels may be non-marketable by-products. The quality of these fuels may vary greatly. Some Gulf Coast refineries purchase natural gas as a clean fuel source.

Approximately 5 to 10 percent of the heating value of crude oil processed at a refinery is consumed for refinery heat production. Heat requirements range from 218,000 to 435,000 Btu's per bbl (460,000 to 920,000 Kcal per m³) of crude. Steam production uses approximately 138,000 Btu's per bbl (292,500 Kcal per m³) of crude. Water fed to steam production units is usually treated with anti-corrosives, such as chromates or zinc compounds.

- o Process description: Fuels are usually burned to heat process materials and steam is usually produced in fired boilers serving several points of use. The catalytic cracking-associated carbon monoxide boiler may be a major heat source for steam.
- o Products: Heat and steam.

- o Operating parameters: Temperatures at 1,832 to 2,732°F (1,000 to 1,500°C), and pressure at 500 psig (35 kg per cm²) for steam production.
- o Wastes: For residual oil-fired boilers, industry-wide emissions have been reported to be:
 - (1) Particulates--0.72 lbs per bbl (2.75 kg per m³) fuel;
 - (2) Sulfur dioxide--5 lbs per bbl (19 S kg per m³) (S = percent by weight of sulfur) fuel;
 - (3) Sulfur trioxide--0.06 lbs per bbl (0.25 S kg per m³) fuel;
 - (4) Carbon monoxide--0.12 lbs per bbl (0.5 kg per m³) fuel;
 - (5) Hydrocarbons--0.09 lbs per bbl (0.35 kg per m³) fuel;
 - (6) Aldehydes--0.03 lbs per bbl (0.12 kg per m³) fuel; and
 - (7) Nitrogen oxides--1.25 to 7.5 lbs per bbl (4.8 to 9.6 kg per m³) fuel.

For refinery gas-fired boilers, emissions have been reported to be:*

- (1) Particulates--76 lbs per 10⁶ bbl (290 kg per 10⁶ m³) fuel;
- (2) Sulfur oxides--2.5 lbs per 10⁶ bbl (9.6 kg per 10⁶ m³) fuel (based on 4,600 gr sulfur per 10⁶ m fuel);
- (3) Carbon monoxide--71 lbs per 10⁶ bbl (270 kg per 10⁶ m³) fuel;
- (4) Hydrocarbons--13 lbs per 10⁶ bbl (48 kg per 10⁶ m³) fuel; and
- (5) Nitrogen oxides--60 lbs per 10⁶ bbl (230 kg per 10⁶ m³) fuel.

*Note that emissions from gas-fired boilers are on the order of 10⁻⁴ times those from oil-fired burners.

Aqueous wastes associated with steam production are primarily boiler blowdown, which usually has low oil and phenols concentration and is often reused in other process units with minimal treatment. Solid wastes include ash from boilers and sludges from treatment of steam boiler feed water.

- o Trends: Efforts are being made to reduce energy (fuel) consumption in refineries.

Pressure Relief and Flare Systems

- o Applications: Pressure relief and safety outlets are required to relieve potentially damaging pressures that may build up in equipment, especially during start-ups, shut-downs, and emergency situations. Environmental and safety concerns usually require the use of a closed blowdown or collecting system to catch released materials, although some pressure relief and safety valves may vent directly to the atmosphere. Flares are used to dispose of released gases through combustion.
- o Input materials: Any refinery material (gases and/or liquids) may be released from pressure release and safety valves. Releases sometimes include waste process gases and gases separated from blowdown systems.
- o Process description: Discharged materials are collected and gases and liquids are separated in a knockout drum. Fluids are collected and pumped to oil-water separation/recovery systems. Vapors are passed to a flare supplied with a pilot flame to ensure hydrocarbon combustion. Steam may be injected into the flare to reduce visible smoking. Most flares employ vertical stacks 20 to 300 feet (600 to 9,000 cm) high.
- o Products: recovered oil, water for reuse or processing, and vented and flared gases.
- o Operating parameters: A pilot flame ensures combustion of flared hydrocarbon vapors. Smokeless flaring requires approximately 0.2 to 0.5 lbs of steam per lb of hydrocarbons flared.
- o Wastes: Total flare emissions have been reported to average 120 to 200 lbs per 1,000 bbl crude oil.
- o Trends: Flaring will continue to be a useful method for disposing of pressure released hydrocarbon emissions. More

attention may be paid to the design and functioning of pressure relief systems as they may be a major source of fugitive air emissions.

Blending and Packaging

- o Application: Blending of refinery intermediates and products produces marketable products with desired qualities. Packaging places final products in containers for marketing and consumption by industry, retailers, and consumers.
- o Input materials: Various refinery products and additives.
- o Process description: Blending may be performed in a single tank or by in-line mixing in a header. In-line blending is most commonly used for final products and tank blending is used for feedstocks and intermediates. Storage-blending tanks may be dedicated to a single operation or switched as needed.
- o Wastes: Fugitive hydrocarbon and other emissions associated with product storage and transfer may occur during blending. Tetraethyl lead and other additives are highly toxic and require care in handling. Sludge from gasoline tanks may be high in lead content.
- o Trends: Automation of blending and packaging is a continuing trend, along with contract packaging of lesser-volume products.

Crude Oil and Product Storage*

- o Applications: Crude oils are stored to provide adequate feedstocks for economical use of refining facilities. Storage of intermediate products equalizes material flows within the refinery. Final products storage is used to store finished products prior to shipment, to mix and blend products, and to lessen the effects of product demands on refinery operations.

Typical refinery crude oil storage is 2 weeks to 2 months of supplies. Storage allows for the settling-out of water and suspended solids.

*Storage technology and emissions are discussed in the Transportation and Storage section of this report.

- o Input materials: Crude oils, intermediates, and final products.
- o Products: Crude oils, intermediates, and final products. (Settled-out water and solids are usually removed.)
- o Process description: Crude oil and intermediate and final products are stored in steel tanks ranging in size from several thousand barrels to several hundred thousand barrels capacity. Settled water and suspended solids are drawn off periodically. Many tank storage systems employ methods to minimize releases of hydrocarbon vapors such as floating-roof tank covers, tank pressurization, and/or connections to vapor recovery systems.
- o Operating parameters: Pressure is atmospheric or greater and the temperature is ambient.
- o Wastes: Free and emulsified oil, as well water and suspended solids, are drawn off into the wastewater treatment system. Bottom sludge and sediments are removed less frequently and are generally disposed of in landfills or by landspreading. Leaks, spills, and tank cleaning produce additional wastes.

Intermediate storage may be a source of polysulfide-bearing wastewaters and iron sulfide suspended solids. Final product storage wastewaters may contain tetraethyl lead and other additives.

- o Trends: Many refineries are instituting hydrocarbon vapor release minimization systems. Floating-roof covers will become more common due to recent regulations concerning volatile organic compounds (hydrocarbon emissions).

Bottom Sediment and Water (BS&W) specifications are imposed on crude oils by many refineries. Increased use of drying processes during intermediate processing reduces wastewater from finished and intermediate products storage.

Wastewater Treatment

- o Applications: Wastewater treatment is used to upgrade used process, runoff, and sewerage waters prior to their discharge into open waters, publically owned treatment works, or their reuse within the refinery. Refinery wastewaters typically contain oil, grease, dissolved and suspended solids, phenolic compounds, ammonia, chromium, sulfides, and other compounds for which effluent levels have been set by Federal, state,

and local laws. Some refineries totally recycle their process water. This requires removal of oil and solids and the adjustment of water quality parameters such as pH to minimize fouling and corrosion.

- o Input materials: Wastewater streams result from water used in various processes. Most wastewater results from condensed steam, sour water stripping, spent caustic solutions, cooling tower and boiler blowdown, acid/alkaline waste neutralization, and process-associated, in-plant water pretreatment processes. Water usage may vary from 5 gallons per day per barrel of crude in newer refineries to over 1,000 gallons per day per barrel of crude in older refineries (Sittig 1978). Various streams, such as process water, cooling water, wash water, sewer runoff, and cooling tower blowdown, may be processed separately or combined for treatment.
- o Process description: Pretreatment or primary wastewater treatment usually involves the separation of oils and settleable solids from the wastewater. API separator units, corrugated plate interceptors, and primary settling ponds are used for oil, oily sludge, and grit removal. Gravity separation forms the physical basis for these units. Flocculation, involving the addition of organic particles to which oil and particles adhere, is used in some refineries. Common flocculants are alum and polyelectrolytes, which are high-molecular-weight, polar, synthetic, water-soluble, organic polymers. If process wastewaters are excessively acidic or alkaline, they must be neutralized. Acidic and basic waste streams may be mixed or ammonia, lime, limestone, or soda ash used to neutralize acidic streams. Sulfuric acid, hydrochloric acid, flue gases containing carbon dioxide, or sulfur may be used to neutralize alkaline streams.

After pretreatment, suspended solids are usually removed by sedimentation or air flotation. Sedimentation involves gravity separation (settling) of particulate matter. Dissolved air flotation involves saturation of wastewater with air under pressure (approximately 40 psig). The release of this pressure causes air bubbles less than 100 microns in diameter to attach to particulate matter and float it to the surface. Dissolved air also aids subsequent biological oxidation of wastes. Screening and filtration may be used for wastewater with a low solids load.

Secondary treatment processes degrade soluble organic matter in the wastewater and reduce the biological and chemical oxygen demand (BOD and COD). Microorganisms catabolize or metabolically degrade most soluble organics, eventually to carbon dioxide, nitrogen, and

water. Secondary treatment processes include activated sludge, trickling filter, aerated lagoon, unaerated lagoon, and anaerobic treatments. Unaerated lagoons are the simplest, but require large land areas and have lower capacities. Aerated lagoons involve mechanical aeration or oxygenation and mixing. Trickling filter processes involve wastewater flow and contact with microorganisms growing on solid media such as beds of rocks, polyvinyl chloride packings, or rotating partially submerged discs (Bio-Disk process). Anaerobic treatments such as stabilization ponds are not commonly used because sulfur dioxide odors result from the anaerobic bacterial metabolism of sulfur-containing compounds. Sludge is a by-product of secondary treatment processing.

Tertiary treatment processes may be applied to remove special pollutants or to comply with effluent or recycled water standards. Chlorination, ozonation, ion exchange, membrane separation (e.g. reverse osmosis), activated carbon and other types of filtration, coagulation, oxidation, and flotation processes may be employed. Chlorination is probably the most commonly used process for final chemical wastewater treatment. Calcium hypochlorite, sodium hypochlorite, and pure chlorine may be added to the effluent stream. Ion exchange resins can remove significant amounts of phosphates, nitrates, ammonia, and chromates. Activated carbon absorption preferentially removes large, non-polar organics. Granular media filters, using combinations of sand, coal (anthracite), activated carbon, garnet, and resin beds, are currently in use. Membrane separation processes based on reverse osmosis, electrodialysis, ultrafiltration, and microfiltration provide a means for concentrating the wastewater stream.

Final effluent disposal is accomplished by direct discharge, controlled discharge from holding ponds, or eventual discharge from a series of aerated lagoons. Zero discharge may be achieved through use of evaporation ponds and extensive water recycling.

Wastewaters to be recycled for process water may require oxidation to remove remaining phenols, nitrates, and ammonia, and may require cooling to remove heat. Cooling-oxidation processes include spray ponds, air stripping, autooxidation, and cooling towers.

- o Products: Water containing lesser amounts of pollutants for discharge or reuse, various waste streams, and settled or filtered sludges.
- o Operating parameters: Most wastewater processing is done at ambient temperature and pressure.

- o Wastes: Atmospheric emissions consist primarily of hydrocarbons released from the collection system and primary treatment units. Typically, approximately 16 to 17 percent by volume of the oil in an API separator vaporizes. Separators frequently are not sealed due to explosive hazards, but floating insulating materials on the oil can reduce fugitive emissions to approximately 2 percent by volume.

Primary treatment produces solid wastes in the form of dirt, grit, oily sludges, and clarifier sludges. Secondary treatment produces bacterial sludges. These solid wastes are usually landfilled or landspread. Bacterial sludges may be incinerated and the resulting ash landfilled.

- o Trends: All refineries perform primary treatment to remove oils and solids. Most utilize some form of secondary biological treatment, although some may use deep well disposal or chemical oxidation processes (oxidation with ozone, chlorine, or permanganate).

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HAZARDS OF REFINERY OPERATIONS

Occupational Health

Trends in Petroleum Refining Affecting Safety and Health

Major technological changes in petroleum refining have had significant impacts on refinery employment (U.S. Bureau of Labor Statistics 1979). Computer control and advanced instrumentation, improved processes, and a trend toward larger refineries and consolidation of functions are among the factors that have contributed to an average annual productivity rise of 4.3 percent in petroleum refining from 1960 to 1977, compared with 2.6 percent in all manufacturing. This productivity rise is expected to continue through 1985, but at a slower pace.

A number of process-related trends will affect health and safety in refineries. Increased fluid catalytic cracking, hydrotreating to process sour crudes, and reforming, alkylation, and isomerization to increase gasoline octane ratings add potential health and safety hazards. The decrease in the use of lead-based additives to increase octane ratings and the increase in use of petroleum-derived fractions as petrochemical feedstocks are leading to increases in the use of catalytic reforming and aromatic extraction units, which yield process streams and products with higher concentrations of more toxic, higher-octane, aromatic hydrocarbons. Increased usage of higher sulfur crude oils results in accelerated corrosion and deterioration of refinery equipment, more hydrogen sulfide, and other safety hazards.

Some sources have charged the petroleum refining industry with misplaced priorities regarding health and safety (Engler 1975). Equipment run times have increased, turnarounds (periods when a unit is shut down for cleaning and repair) have been shorter and less frequent, and poor preventive maintenance and testing have been noted in some refineries. With increases in the prices obtained for refined products and the nation's needs for these products, it may be more economically attractive to run equipment until it fails, rather than to perform preventive maintenance. Government regulations, high interest rates, a long-run projected decline in the rate of growth of product demand, and other factors have been cited as disincentives for large capital investments and improvements by refineries.

On the other hand, better on-stream inspection techniques, newer and better materials, advanced instrumentation and control, corrosion-reducing additives, and experience and advances in refining allow longer run times and minimize potentially hazardous start-ups, shutdowns, and routine maintenance.

Refinery employment is expected to decline to approximately 137,000 employees in 1985--for a drop of 1.9 percent annually from 1977 to 1985 (U.S. Bureau of Labor Statistics 1979). Newer and modernized refineries employ fewer workers than comparable older facilities. Cross-crafting, or the consolidation of various maintenance and operating job functions, also reduces manpower requirements. Contracting out many tasks is another trend contributing to lower refinery full-time payrolls. Many of these contract employees perform hazardous tasks and should not be forgotten when one considers health and safety hazards in refineries.

The reduction in the number of employees in processing areas may have several implications for plant safety. Fewer workers may be available for fire fighting and handling emergencies. Leaks, spills, and dangerous situations may tend to remain unidentified. Essential work may be delayed as fewer men are available to perform essential tasks.

Workers Employed in Refineries

The number of workers employed in refining operations in 1978 was 81,168, according to the American Petroleum Institute (1979b). Union sources estimate the refining industry total at about 135,000, of which about 75,000 are considered production workers. The approximately 55,000 non-production workers include clerical, managerial, and technical workers not directly working with refinery equipment. These non-production workers should not be included with refinery production workers when one considers most occupational hazards. However, they work within the confines of the refinery and may be exposed to airborne toxic chemicals and catastrophic events. Other workers, such as contractor employees, construction workers, part-time employees, and truck drivers, may work within the processing area of the refinery and also may be exposed to its hazards.

A recent final Environmental Impact Statement (EIS) for a proposed 175,000 bbl-per-day refinery at Portsmouth, Virginia, contains the following information regarding employment (U.S. Army Corps of Engineer 1977):

- o The refinery will employ 350 persons, with an additional 150 employees involved in terminal, storage, and attendant operations.
- o Employment is anticipated to be 90 percent male.
- o The majority of workers are in skilled categories: pipefitters, welders, boiler makers, electricians, technicians, and laboratory workers.

- o In the typical refinery, 60 percent of the workforce would be classified as production workers and the remainder would be in support capacities.
- o Approximately 10 percent of the employees have managerial or highly technical (engineering) responsibilities.

These data are probably applicable to most larger, modern refineries.

Recognition of Refinery Occupational Hazards

There is a general lack of published occupational health studies involving refinery workers, despite the large number of known and suspected toxic chemical and physical hazards, including carcinogenic and neurotoxic agents, to which refinery workers are potentially exposed. The reader is referred to a recent review for a discussion of epidemiological studies to date (Bingham et al. 1980). The Basic Effects Issues section of this report offers further information on potential chemical hazards and adverse effects that may be associated with refineries.

Available epidemiological studies do not present a consensus or support conclusions regarding excesses and causes of refinery workers' morbidity and mortality. These have focused mainly on the risks of developing cancer, especially excessive cutaneous, pulmonary, and digestive tract cancers from benzo(a)pyrene and other PAHs which are constituents of crude oil, residuals, soots, and refinery air emissions (Darby et al. 1978).

Data concerning refinery occupational injuries and illnesses reported annually to the Occupational Safety and Health Administration (OSHA) for 1978 are presented in Table 1 of the Offshore section of this report. The data indicate that refining is one of the more hazardous aspects of the petroleum industry.

Available general population epidemiological studies do not specifically incriminate petroleum refineries as sources of generalized environmental hazards or carcinogens, but strongly suggest the need for further study and concern. A U.S. survey of lung cancer mortality by county from 1950 to 1969 found higher rates among males in 39 petroleum-industry-intensive counties (Blot et al. 1977). When compared to male residents of 117 demographically similar counties without intensive petroleum-related activity, male residents of petroleum-intensive counties had higher rates for cancers of the lung, nasal cavity and sinuses, and the skin, including malignant melanomas. Higher rates for lung cancer among female residents indicated a possibility of a pollution hazard beyond the workplace. Another study in the Los Angeles area revealed higher lung cancer

mortality rates in areas that were heavily industrialized, including areas with petroleum refineries, and that had higher concentrations of benzo(a)pyrene and other PAHs in soil and air (Menck 1974).

Published occupational health surveys of refinery workers generally have not been available. Several evaluations of isolated health hazards within refineries have been performed by the National Institute for Occupational Safety and Health (NIOSH) and the Institute is currently completing nine industrial hygiene surveys characterizing worker exposures to polycyclic aromatic hydrocarbons in petroleum refineries. Overall, except for studies on specific problems, little information is available concerning the health of refinery workers.

Hazardous Exposure Monitoring

Little published worker exposure information is available. Industrial hygiene monitoring primarily involves measurement of concentrations of substances in air and sometimes extrapolated measurements of personal exposures obtained from toxic substance-adsorbing dosimeters carried by workers. Potential hazards that have been monitored include noise, hydrogen sulfide, asbestos, benzene, hydrocarbons, and tetraethyl lead. Other hazards that constitute clear acute toxic hazards, which must be monitored in compliance with Federal or state laws, or which have been recognized as potential hazards on the part of refinery management, presumably also are monitored.

As discussed in other sections, many hazardous substances are known to be used within refineries. A 1977 survey of refineries by the U.S. Environmental Protection Agency (EPA) provides data regarding purchases and manufacture of EPA Priority Pollutant Compounds. The number of U.S. refineries handling these is shown in Table 6. Exposures to these hazards may occur among workers as a result of ignorance, negligence, unscheduled events and accidents, improper design, or faulty equipment.

Chronic exposure to low levels of many toxic substances is a likely situation among refinery workers. Little is known of the synergistic, antagonistic, carcinogenic, teratogenic, fetotoxic, neurological, and other toxic effects and interactions among the numerous substances to which refinery workers may be exposed.

Many exposures to toxic substances are difficult to assess and quantify, especially those received via contact and subsequent percutaneous absorption or ingestion. Measurement of toxic materials in respirable air does not fully account for all toxic exposures.

TABLE 6
EPA PRIORITY POLLUTANT CHEMICALS^a

Priority Pollutant	Number of Refineries That Purchase The Chemicals as a Raw or Intermediate Material	Number of Refineries That Manufacture The Chemicals as a Final or Intermediate Material
Acenaphthene	9	8
Acrolein	1	0
Acrylonitrile	2	0
Benzene	42	62
Carbon tetrachloride	30	2
Chlorobenzene	0	0
1,2-Dichloroethane	6	0
1,1,1-Trichloroethane	26	2
Hexachloroethane	1	0
1,1-Dichloroethane	2	0
1,1,2-Trichloroethane	4	0
1,1,2,2-Tetrachloroethane	1	0
Chloroethane	1	0
2,4,6-Trichlorophenol	1	0
Chloroform	9	0
2-Chlorophenol	2	0
1,2-Dichlorobenzene	2	0
1,3-Dichlorobenzene	0	0
Dieldrin	1	2
Benzidine	0	4
P-chloro-m-cresol	0	0
1,4-Dichlorobenzene	0	0
1,4-Dichloroethylene	6	0
1,2-Trans-dichloroethylene	2	0
2,4-Dichlorophenol	0	0
1,2-Dichloropropane	6	0
1,3-Dichloropropylene	3	0
2,4-Dimethylphenol	9	11
Asbestos	18	0
Ethylbenzene	24	31
Fluoranthene	13	11
Methylene chloride	2	0
Methyl bromide	1	0
Trichlorofluoromethane	12	0
Dichlorodifluoromethane	9	0
Phenol	32	32
Bis(2-ethylhexyl) phthalate	1	1

TABLE 6 (Continued)

Priority Pollutant	Number of Refineries That Purchase The Chemicals as a Raw or Intermediate Material	Number of Refineries That Manufacture The Chemicals as a Final or Intermediate Material
Butyl benzyl phthalate	1	1
Di-n-butyl phthalate	1	1
Diethyl phthalate	1	1
Dimethyl phthalate	1	1
PCB-1242	1	0
PCB-1254	1	0
1,2-Benzanthracene	14	12
Benzo(a)pyrene	14	12
3,4-Benzofluoranthene	10	12
11,12-Benzofluoranthene	10	12
Chrysene	16	14
Acenaphthylene	11	12
Anthracene	16	14
1,12-Benzoperylene	14	12
Fluorene	10	12
Phenanthrene	16	14
Naphthalene	18	18
Nitrobenzene	1	0
Pentachlorophenol	10	1
4-Nitrophenol	1	0
Methyl chloride	1	0
Isophorone	0	1
1,2:5,6-Dibenzanthracene	11	12
Indeno (1,2,3-C,D)pyrene	11	12
Pyrene	16	14
3,2,7,8-Tetrachlorodibenzo-p-dioxin	0	1
Tetrachloroethylene	2	1
Toluene	53	53
Trichloroethylene	12	0
Vinyl chloride	0	0
Antimony and compounds	8	1
Arsenic and compounds	6	1
Zinc and compounds	71	6
Beryllium	0	0
Cadmium and compounds	4	0
Chromium and compounds	80	5
Copper and compounds	26	1
Cyanides	1	20

TABLE 6 (Concluded)

Priority Pollutant	Number of Refineries That Purchase The Chemicals as a Raw or Intermediate Material	Number of Refineries That Manufacture The Chemicals as a Final or Intermediate Material
Lead and compounds	121	9
Mercury and compounds	5	0
Nickel and compounds	21	6
Selenium and compounds	2	1
Silver and compounds	6	1
Thallium and compounds	1	1

^aIncludes chemicals reported as purchased or manufactured by 253 refineries surveyed.

Source: U.S. Environmental Protection Agency 1979b.

Several of the hazardous materials handled within the refinery are liquids or solids--and the frequency, amounts, and severity of worker exposure to the intake of liquids and solids are difficult to assess. Workers may be exposed to hazardous materials via contact with liquids on solid surfaces (ladders, valves, and railings). Many exposures are likely to occur during maintenance, from leaks and spills, during start-up and shutdown operations, and from contact with materials condensed or splashed on surfaces.

Biologically-based methods for monitoring an individual worker's exposures through measurement of substances or their metabolites in body fluids, excretions, and hair are available only for a limited number of toxic substances. The extent of biologically-based monitoring in the refining industry is unknown.

Carcinogens in the Refinery

The EPA's Carcinogen Assessment Group recently identified 150 chemicals as carcinogens (Inside Washington Publishers 1980). Many of these, shown in Table 7, are likely to be encountered in varying amounts in the refinery.

Condensed and settled solids and liquids on refinery surfaces and workers may contain appreciable amounts of PAHs. PAHs concentrations from an apron worn by a petroleum coking unit worker are shown in Table 8.

Other Refinery Hazards

Hot Environments. Heat stress among refinery workers has been documented (Hervin et al. 1973) since considerable amounts of heat radiate from process equipment.

Confined Areas. Workers in confined areas, such as those performing periodic maintenance in boilers, tanks, exchangers, and reaction chambers, are potentially exposed to a number of hazardous vapors, including asphyxiants such as hydrocarbons, carbon dioxide, and steam, and toxic substances such as volatilized lead additives, PAHs, and other hydrocarbons. Explosions may occur in confined areas. Moreover, solid and liquid wastes removed from equipment in confined areas may pose hazards for workers.

Catalysts. The exact nature of the catalysts employed in petroleum refining generally are proprietary or trade secrets. However, some catalyst types and their uses are identified in Table 9. Many of these catalysts are fixed on powdered or granular alumina, silica, or other substrates. Several pose hazards when they are inhaled or come in contact with the skin or eyes. The Doctor Sweetening process for converting thiols to disulfides (being replaced by other

TABLE 7

EPA-DESIGNATED CARCINOGENS LIKELY TO
OCCUR IN REFINERIES

Polycyclic Aromatic Hydrocarbons

2-Acetylaminofluorene

Benz(c)acridine

Benz(a)anthracene

Benzo(b)fluoranthene

Benzo(j)fluoranthene

Benzo(a)pyrene

Chrysene

Dibenz(a,h)acridine

Dibenz(a,j)acridine

Dibenz(a,h)anthracene

Dibenzo(a,h)anthracene

7H-Dibenzo(c,g)carbazole

Dibenzo(a,e)pyrene

Dibenzo(a,h)pyrene

Dibenzo(a,i)pyrene

7,12-Dimethylbenz(a)anthracene

3-Methylcholanthrene

Benzene

Coke oven emissions

Metals

TABLE 7 (Concluded)

Cadmium and compounds

Chromium and compounds

Nickel and compounds

Nickel carbonyl

Ethylene bis dithiocarbamate

Aldehydes

Formaldehyde

Glycidyl aldehyde

Nitrosamines

N-Nitrosodiethanolamine

N-Nitrosodiethylamine

N-Nitrosodimethylamine

Soots and Tars

2,3,7,8-Tetrachlorodibenzo-p-dioxin

2,4,6-Trichlorophenol

TABLE 8

POLYNUCLEAR AROMATICS ON A
REFINERY WORKER'S APRON

PAH	Quantity in 1/2 Apron (Mmg)	Quantity in Swatches (Mmg)
Pyrene	1,000	
Benz(a)anthracene	790	950
Chrysene	560	
Triphenylene	370	
Bethyl benz(a)anthracene	1,120	
CM/ET benz(a)anthracene	530	
Benzo(a)pyrene	840	1,300
Benzo(e)pyrene	1,130	
Benzo(g,h,i)perylene	420	
Methyl benzo(a)pyrene	400	
Methyl benzo(e)pyrene	1,330	

Source: Venable 1975.

TABLE 9

MISCELLANEOUS REFINERY CHEMICAL HAZARDS

Substance	Uses	Hazards
Acetic acid	Emulsion breaking, polymer extraction, dewaxing, sulfur reduction	Irritant
Acetone	Benzene isolation (azeotropic distillation), lube oil dewaxing	Dermatitis, irritation, narcosis
Aluminum chloride	Isomerization catalyst	Irritant, corrosive
Aluminum oxide (Bauxite)	Cracking catalyst constituent	Pulmonary disease (inhalation)
Barium hydroxide	Treat spent caustic solutions; neutralize acid treated oils	Caustic, heart disorders
Cadmium compounds	Desulfurizing, lube oil additives	Highly toxic; respiratory irritant; pulmonary edema; dyspnea; emphysema; kidney damage
Chlorine	Disulfides oxidation; bentonite clay regeneration	Eye inflammation; pneumonitis; pulmonary edema; fatal above 1,000 ppm
Absorbents: alumina, bauxite, silica gel, bentonite, diatomaceous earth, activated carbon	Improve color, odor, stability of waxes and lube oils	Irritation; inhalation hazards

TABLE 9 (Continued)

Substance	Uses	Hazards
Copper chloride	Convert mercaptans to insoluble disulfides (sweetening)	Skin irritation; liver cirrhosis
Dichloroethyl ether	Chlorex extraction--improve yield and viscosity of highly paraffinic oils	Strong irritant; nausea; eye damage, liver disorder-death
Ethanolamines: monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA)	Extraction of water, H ₂ S, CO ₂ from gaseous streams	Skin and eye irritation; nitrosamine precursors
Ethylene dichloride (1,2-dichloroethane)	Solvent extraction--wax removal from lube oils	Dermatitis; serious eye damage; liver and kidney damage; carcinogenic
Ethylene glycol	Solvent extraction (Udex Process)	Irritation (skin, eyes, mucous membranes)
Furfural	Solvent extraction of distillate fuels (removes low octane number and other substances) and lube oils	Irritation (skin, eyes, mucous membranes); contact dermatitis; photosensitivity
Hydrogen fluoride	Alkylation catalyst	Extremely corrosive and toxic; burns wherever contact occurs; may cause death over 50 ppm (air)
Hydrogen	Catalytic reforming	Explosive
Methyl ethyl ketone (MEK)	Solvent dewaxing of lube oils	Irritant (eyes, mucous membranes); dermatitis; narcosis

TABLE 9 (Continued)

Substance	Uses	Hazards
Methyl isobutyl ketone	Deoiling of refined waxes	Irritant (eyes, mucous membranes); dermatitis; narcosis; similar compound (n-butyl ketone) implicated in polyneuropathy
Nitrobenzene	Nitrobenzene extraction of lube oils; increase viscosity and extract carbon and sludge-forming compounds	Eye irritant; methemoglobinemia and other blood disorders; liver disorders from chronic exposure; nitrosating agent
Phosphoric acid, copper pyrophosphate	Polymerization catalysts	Corrosive; irritant
Propane	Solvent extraction-deasphalting, dewaxing, decarbonizing	Flammable gas; asphyxiant; narcotic effects
Sodium hydroxide (caustic soda)	Caustic washing-removal of acidic substances, including naphthenic acids, phenolics, H_2S , mercaptans	Extremely corrosive; blindness
Sodium hypochlorite	Sweetening gasoline fractions	Irritant; corrosive
Sodium plumbite	Doctor sweetening	Lead poisoning
Sulfur dioxide	Extraction of aromatic hydrocarbons and sulfur compounds	Irritant; corrosive, asphyxiation of some hypersusceptible individuals, co-carcinogen

TABLE 9 (Concluded)

Substance	Uses	Hazards
Sulfuric acid	Extraction of resinous materials, asphaltic substances, mercaptans	Highly corrosive to any tissue contacted
Trichloroethylene	Lube oil dewaxing; extract carbon- and sludge-forming constituents of lube oils and increase viscosity	Carcinogenic; kidney disorders; irritant and narcotic vapors

Source: Adapted from DeNora and King 1967; Sittig 1979.

processes) employs a solution of sodium plumbite, a water-soluble lead salt. Platinosis has been discussed as a potential health hazard. Platinum can promote mutagenicity and carcinogenicity.

Dyes. Numerous oil-soluble dyes are added to gasoline and other refinery products in concentrations of up to five ppm. Dyes impart characteristic colors to facilitate identification of different grades, products, and brands. Dyes added to aviation fuel include: 1,4-bis (alkylamino) anthraquinones (blue); methyl derivatives of 4-(phenylazo)-2-naphthols (red); (phenylazo)-2-naphthols (orange); and N,N-dimethyl-4-(phenylazo) benzeneamine (yellow) (Darby et al. 1978). These aromatic amine compounds may be carcinogenic, as are many other aromatic amine dyes with similar structures.

Asbestos. Considerable amounts of asbestos are used within refineries for insulation. Workers handling or working near this material may inhale asbestos fibers, certain types and sizes of which are carcinogenic. Potential risks from asbestos inhalation might be lower for refineries than for many other establishments due to the outdoor nature of refineries.

Refinery-Associated Skin Disorders

Skin Diseases--General Incidence. Skin diseases of occupational origin outnumber all other work-incurred illnesses (Birmingham 1978). Between 1940 and 1970, records compiled by state health departments and compensation boards show that skin disorders accounted for 60 to 80 percent of all reported occupational diseases. Bureau of Labor statistics for 1972 show that skin disorders caused 41 percent of the total 210,500 occupational disease cases and 25 percent of all lost workdays.

Chemically-Induced Skin Disorders. Contact with oils may cause several types of severe skin disorders: contact dermatitis, folliculitis, photosensitization, irritation, and skin cancers. Additives in petroleum products and exposures to processing chemicals also may exacerbate or cause skin disorders.

Primary irritants cause direct injury to skin tissues. Most oils and petroleum products cause varying amounts of irritation on prolonged contact. Contact dermatitis disorders may be caused by irritation or contact sensitization. Contact sensitization (less frequent than irritant-mediated dermatitis) involves the development of acquired allergic reactions to substances. Once an individual has developed antibodies after initial exposure to an antigenic substance, subsequent contact induces allergic reactions, primarily contact dermatitis, which are apt to be more severe and prolonged than irritant-mediated dermatoses. Examples of cutaneous sensitizers include poison ivy, poison oak, nickel salts, and formaldehyde.

Photosensitization involves the interaction of photoreactive substances with light to produce conditions that induce dermatitis. Various constituents of crude oil and residual fractions (e.g., asphalts and residual fuel oils)--phenanthrene, anthracene, and acridine--are known photosensitizers. Photosensitization among workers in an asphalt blowing unit has been documented (Vandervort and Lucas 1974). Hyperpigmentation may also be caused by contact with photosensitizers.

Acute contact dermatitis causes a number of signs and symptoms including redness, swelling, blistering, oozing, itching, burning, and general discomfort. Acute contact dermatitis can occur anywhere on the skin. Chronic dermatitis may involve marked dehydration leading to skin thickening, scaling, and cracking and fissuring of the digits and palm.

Folliculitis and acne may be caused by chronic contact with water-insoluble oils, especially crude oils, lubricating oils, asphalts, and greases. These disorders are caused by blockage of sweat ducts at the base of hair follicles.

Skin cancers may result from contact with crude oils or refinery products. Several PAHs in oil and petroleum products are known skin carcinogens. Refinery and storage facility workers are exposed to the major cause of skin cancer, sunlight, due to the outside nature of their work. The combined effect of exposure to sunlight, hydrocarbons, and other hazardous agents may present an added health risk to these workers.

Occupational Safety

Safety in Design and Operation

Petroleum refineries represent tremendous investments and have large, powerful components that continuously handle hazardous materials at high temperatures and pressures. Refinery design and process technologies are well developed, proprietary, and highly competitive. Safety, both for the physical plant and worker, is a major factor in refinery design and operation (Barber 1975).

Refinery safety factors presumably incorporated in the design phase include:

- o Plans to isolate hazardous.
- o Access to and egress from equipment during normal, maintenance, and emergency operating conditions.

- o Safe design of mechanical equipment. Workers require protection from moving parts and hot surfaces.
- o Safe design of electrical equipment. Proper grounding, circuitry, insulation, and isolation are required for electrical safety and to control potential ignition sources.
- o Selection of corrosion-resistant materials.
- o Preventive analysis of vibrations. Components and process units, both large and small, may be subject to destructive vibration.
- o Allowance for pressure failures. Pressure-relieving valves and the discharge of excess materials to safe places are required. Both automatic and manual relief valves and controls are also required.
- o Noise control. Acceptable noise levels and controls should be specified.

Fire safety features incorporated into the refinery design include:

- o Plans to minimize spread of fires and damage to adjacent units. Safe access to critical areas, equipment, valves, and controls is also required.
- o Design of control centers. Process control centers should be in safe areas, blast-resistant, sealable, and have an auxiliary air supply system.
- o Safe electrical equipment. Where hazardous concentrations of flammable vapors may be present, equipment is enclosed in a housing capable of withstanding an internal explosion without igniting outside vapors.
- o Fireproofing of important structures.
- o Surface drainage. Drainage systems should carry spills, fire fighting water, and storm waters away from process units. Impounding basins should be away from storage tanks and process units.
- o Thermal insulation.
- o Water supply and distribution systems for fire fighting. An independent, continuously pressurized fire fighting water distribution system is maintained.

- o Fixed large volume water nozzles and sprayers. In case of fire, fixed water nozzels that are controlled automatically, manually, and/or remotely, are trained on equipment that is known to be unsafe.
- o Vapor detection devices. Vapor detectors should monitor unattended, potentially hazardous equipment, such as gas compressor houses.
- o Fire detection devices. These are linked to alarm systems and/or activate fixed fire extinguishing equipment.
- o Special fire control systems. Certain equipment and situations may require installation of foam, dry chemicals, halogenated gases or liquids, or other fire fighting or suppressant systems.

In addition, some refineries require special fortification against earthquakes, hurricanes, and other natural disasters. Refineries and storage facilities in earthquake-prone areas of the U.S. such as California have survived damaging earthquakes without sustaining major losses.

Industry sources report that the majority (up to 80 to 90 percent) of injury-causing accidents are the result of personnel failures in operating or maintenance practices. Extensive training programs are conducted at many refineries to inform workers about their particular job and its place within the total refinery operation.

Petroleum refining is an area in which process control instrumentation and automation are becoming a highly advanced and utilized technology. Instrumentation and automation tend to increase safety by permitting remote and real-time supervision and increased control of refinery operations. Process control instrumentation and automation also permit the optimization of products and energy usage.

Fires and Explosions

Petroleum refineries handle vast quantities of combustible hydrocarbons and reactive substances that are frequently subjected to high temperatures, pressures, and are nearly always confined. Fires and explosions may kill or injure refinery workers and fire fighters, cause considerable property damage, disrupt vital refinery operations, endanger neighboring industrial and residential communities, and may release toxic materials to the atmosphere.

Fires are usually classified by the financial losses they cause. American Petroleum Institute (API) data indicate that, during 1974 to 1975 for 83 refineries, 61 fires each caused a loss greater than \$100,000, and 19 each caused a loss greater than \$500,000 (Health and Safety Executive 1980). United Kingdom (U.K.) Fire Research Station statistics for the years 1972 to 1973 indicate that, of 22 refineries, 10 had fires resulting in losses of more than \$50,000. Ratios for fires causing losses on the order of \$50,000 to \$100,000 are about one in five per year in the U.S. and one out of four in the U.K.

API and U.K. data are not readily available on the incidence of deaths from fires and explosions, or on the incidence of explosions, either as a cause or aftermath of fire (Health and Safety Executive 1978). A Canvey Island risk assessment study concluded from available data that about 50 percent of large refinery fires might be accompanied by some form of explosion, i.e., the ignition of a cloud of flammable vapor, whether confined or unconfined. The study cited data indicating that six unconfined vapor cloud explosions occurred among the world's 600 refineries in a recent 10-year period (Health and Safety Executive 1978).

Some processes such as hydrotesting involve a feed of highly flammable hydrogen into large pressurized vessels. Explosion is possible if air enters the reaction chamber. In 1955 a hydroformer at Whiting, Indiana, exploded, scattering fragments over a wide radius. Fragment projectiles impacted on storage tanks causing leakage and widespread fires (Health and Safety Executive 1978). Leaks, especially of gases, may cause explosions.

Hydrocracking and hydrotreating have the greatest potential for accidents, in terms of frequency and severity, of any current refining process units (Bliss et al. 1976). Catalytic reforming and cracking units are the next source of major accidents. Alkylation units have a better accident record. Because volatile, heavier-than-air hydrocarbons can be involved in alkylation unit accidents, larger areas may be affected by fires and explosions.

Explosions may result from overheating of trapped vapors in tanks, piping, valves, and process units. The violence of failure is apt to be greater, but less frequent, in thicker process containers and in piping that handles higher pressures. Violently escaping vapors and liquids may extinguish themselves temporarily, collect, and then reignite, often explosively, after an interval that typically lasts 1/2 to 1 minute (Health and Safety Executive 1978). Shortages of cooling water, corrosion, wear, furnace collapse, environmental conditions, equipment failure, and human error are among the possible causes of fires and explosions.

The refining industry exerts considerable effort in plant design and maintenance, process instrumentation, and employee training to minimize the number and extent of refinery fires and explosions. The frequency of refinery fires and explosions may be expected to rise, as most American refineries age and few are decommissioned. The required large capital investment, industry's view that Federal regulations are inconsistent, taxation, uncertainty of crude oil supplies and product markets, and environmental permit constraints are among the factors cited as disincentives for domestic refiners to replace old facilities or build additional refining capacity.

Some statistics concerning fires at refineries are presented in Table 10. Note that the incidence of refinery fires spreading to other facilities is low.

Refinery and storage facility fires and explosions may cause a number of adverse secondary health, safety, and environmental effects. Oil fires are likely to produce significant atmospheric emissions of pollutants associated with incomplete hydrocarbon combustion: hydrocarbons, sulfur oxides, nitrogen oxides, carbon monoxide, PAHs, and particulate matter. Nearby areas may be exposed to hazardous concentrations, especially if an atmospheric inversion coincides with the fire. Neighboring homes and industrial areas may require prompt evacuation. Abandonment by workers of endangered areas without following proper shutdown procedures and physical damage from blasts and fires may endanger other process units or cause significant spills and emissions of oil and process chemicals.

Refinery and storage facility explosions and fires may cause lengthy shutdowns. Economic dislocations for petroleum companies, insurers, workers, and the local economy may result. Coincident shutdowns at several refineries or storage facilities, whether due to accidents or sabotage, could result in shortages of refined petroleum products on a national scale. The economic and political significance of refining and storage facilities are bound to increase as world demand and prices for crude oil and refined products increase.

The Canvey Island Investigation

The Health and Safety Commission of the British government has recently released the results of an investigation of potential hazards and risks associated with industrial development in the Canvey Island area (Health and Safety Executive 1978). Canvey Island, an island in the Thames River, has a population of 33,000 and intense petrochemical activity. The island is 2.5 miles wide by 9 miles in length. Within this small area are two large petroleum refineries, building sites for two more, several liquified natural gas (LNG) facilities, petroleum product and crude oil tank farms (besides those

TABLE 10
PETROLEUM INDUSTRY FIRE LOSSES^a

	1969	1974	1975
Fire losses (\$ million)	13.8	26.7	73.8 ^b
Total property damages (\$ million)	193,333	209,631	211,080
Total number of fires	541	390	490
Total refinery fires	160	138	186
Spread to other property	0	1	1
Origin outside but spread to refinery	1	0	0
Tankers and barges ^c	2	2	2
Tank farms ^c	4	5	5

^aFor 1970 to 1973, data is not available.

^bHigher value of inventory is reflected in this loss compared to 1969 or 1974.

^cAll confined to company property.

Source: Health and Safety Executive 1978. (Data for 1969 from American Petroleum Institute 1971; 1974 and 1975 from American Petroleum Institute 1974, 1975.)

associated with the refineries), and an ammonium nitrate production facility. In addition, much ship traffic passes close by. Material transfer by ship and pipeline occurs at most of these facilities.

Quantitative risk assessment techniques were employed to assess the probability of numerous catastrophies occurring and to determine the risks to populations living near these facilities. Risks of fire, explosion, and release of toxic agents were quantified to assess the hazards associated with current facilities and with the addition of two more large refineries. The chance of a Canvey Island resident being killed as a consequence of a major accident at the existing facilities was calculated at 5 in 10,000 per year--about the same as the risk of dying from natural causes for persons 25 to 34 years old. (This risk is in addition to other risks the residents carry.) The societal risk of numbers of casualties from several facilities is shown in Table 11. This table shows, for example, that for Refinery A, there are 7.8 chances in 10,000 for 10 or more casualties among non-employees. Thus, each year there is a 0.078 percent probability of 10 or more deaths among persons in adjacent neighborhoods or plants. These assessed risks depend on a number of factors and may not be relevant to American petrochemical facilities.

Refinery Deterioration

Refinery equipment is often subjected to high temperatures, pressures, corrosive substances, vibrations, and physical stress. Constant maintenance and inspections are required to ensure safe operation of the refinery. Acids and other substances, such as hydrogen sulfide, inevitably corrode metal. Any of the above stresses may lead to leaks or more catastrophic events such as spills, fires, and explosions.

Internal hydrogen attack is a phenomenon causing embrittlement and subsequent cracking of steel, especially in steel pressure vessel walls and piping that handle hydrogen. Atomic hydrogen reacts with carbon in steel to form methane and other gases, or it may accumulate in voids and combine to form molecular diatomic hydrogen. Reaction with carbon causes depletion of the carbon in the metal and eventually large internal pressures and microfissures may develop. The steel's mechanical properties (e.g., tensile strength, hardness, eductility) degrade, and it may eventually crack and blister. Equipment subjected to high pressures may experience catastrophic failure. Steel alloys incorporating metals, such as molybdenum, chromium, vanadium, titanium, and niobium, are less vulnerable to internal hydrogen attack. Acoustical (ultrasonic) and high-frequency radiation absorption testing can be used to detect significant internal hydrogen attack at an early stage. However, some areas will always be inaccessible to such nondestructive testing. Moreover, the required equipment is expensive, and the testing labor-intensive.

TABLE 11

SOCIETAL RISKS DUE TO FACILITIES
ON CANVEY ISLAND, UNITED KINGDOM

Facility	<u>Upper Limit for Probabilities</u>						
	The Number of Chances in 10,000 Per Year						
	That Casualties Will Exceed:						
	10	1,500	3,000	4,500	6,000	12,000	18,000
Refinery A	7.8	5.0	3.6	2.7	1.8	1.2	0.8
Refinery B	1.4	1.1	0.7	0.1	---	---	---
Refinery C (proposed)	2.9	2.2	1.7	1.4	1.1	0.8	0.7
Refinery D (proposed)	1.4	0.9	0.5	0.2	---	---	---
Tank Farm A ^a	3.9	3.1	1.5	0.4	---	---	---

Note: --- Represents zero or rounds to zero.

^aReceives from ships, feeds; utilizes multiple distribution methods.

Source: Health and Safety Executive 1980.

Health Effects of Refinery Chemicals

Hydrocarbons

A number of hydrocarbons can escape from refinery equipment to affect public and environmental health in addition to the health of workers within the plant boundary. Hydrocarbon emissions from refineries result primarily from fugitive emissions from storage tanks, leaks from processing units and transfer operations, and from combustion sources. Scarce data are available regarding hydrocarbon concentrations within and in the vicinity of petroleum refineries. Atmospheric dispersion modeling for large refineries indicates that Federal and state ambient air quality standards for hydrocarbons will be exceeded significantly under worst case conditions. These models indicate that under these conditions, refineries will be in compliance with ambient air quality standards for SO₂, particulates, NO_x, and CO.

Several kinds of hydrocarbons can be emitted from refineries, and in the sections below they will be classified according to the following scheme:

- (1) Acyclic (aliphatic) hydrocarbons--hydrocarbons formed from chains of carbon atoms, with or without branching; may be saturated or unsaturated. Examples are propane, dodecane, and 2-methyl-2-butene.
- (2) Alicyclic hydrocarbons--similar to acyclic hydrocarbons, but containing non-resonant rings of carbon atoms; examples are cyclohexane, 1-methyl-3-cyclohexane, naphthanes, and naphthalenes.
- (3) Aromatic hydrocarbons--benzene and its hydrocarbon derivatives; possess one or more non-fused, six-carbon, resonant ring (benzene) structures. Examples are benzene, toluene, and diphenyl.
- (4) Phenolics--aromatic hydrocarbons with one or more hydroxyl (-OH) groups substituted on an aromatic ring. Examples are phenol, 2,6-xyleneol, and 4-chlorophenol.
- (5) Polynuclear aromatic hydrocarbons--hydrocarbons with two or more fused aromatic rings; may be termed heterocyclic, if component rings contain one or more non-carbon atoms (usually nitrogen or sulfur). Examples are benzo(a)pyrene and phenanthrene.

Acyclic Hydrocarbons

In general, members of the acyclic hydrocarbon series are relatively biologically and biochemically inert. Lower alkanes exert a slight anesthetic and depressant effect on the central nervous system at concentrations in the 5 to 10,000 ppm range, with the exception of methane and ethane. For C₅ to C₇ alkanes (pentane, hexane, and heptane), narcosis, convulsions, and death may result if these are inhaled in high concentrations. Alkenes (olefins) and alkynes (acetylenics) are much more toxic. Methane and ethane produce no significant ill-effects, even at high concentrations in ambient air (except when approaching asphyxiant or explosive levels). At extremely high concentrations, acyclic hydrocarbons, frequently termed "simple asphyxiants," displace inhaled oxygen to cause anorexia and asphyxiation. Depressant effects are especially pronounced during exposure to acetylene, ethylene, and propylene, which have been used as medical anesthetics. Acute toxicities for a number of hydrocarbons are compared in Table 12.

Generally, alkanes from pentane (C₅) through octane (C₈) show increasingly narcotic properties. Acyclics, like most volatile hydrocarbons, irritate the skin and mucous membranes. Contact with hydrocarbons defats and dries the skin, making it more susceptible to irritation. Reported cases of alkane vapor exposure are summarized in Table 13. Since exposure to only one alkane is infrequent, the National Institute for Occupational Safety and Health (NIOSH) has recommended a time weighted average concentration of 350 mg per m³ as the occupational limit for mixtures of pentane, hexane, heptane, and total alkanes. These concentration limits are equal to about 120 ppm pentane, 100 ppm hexane, 85 ppm heptane, or 75 ppm octane. NIOSH also recommends a 15-minute maximum allowable concentration (ceiling limit) of 1,800 mg per m³ either for mixtures or single C₅ through C₈ alkanes (about 610 ppm pentane, 500 ppm hexane, 440 ppm heptane, or 385 ppm octane). These recommended standards are based on the conclusion that acute alkane intoxication involves transient central nervous system depression and that chronic intoxication may involve more persistent neurological disorders.

Acyclics above octane (C₈) are not sufficiently volatile to pose serious vapor inhalation hazards at ambient temperature. In 1976, the American Conference of Governmental and Industrial Hygienists set a threshold limit value (TLV) of 200 ppm for nonane (C₉), based on analogy with other alkanes, rather than on controlled tests or observations.

TABLE 12

ACUTE TOXICITY OF ALIPHATIC HYDROCARBONS

Hydrocarbon	Formula	Health Effects	Concentration (ppm)	Percent of Volume of Air	Subject	Ambient Concentrations (ppb)
Methane	CH ₄	No systemic effects	<100,000	10		1,300-4,000
Ethane	C ₂ H ₆	No systemic effects	<50,000	5	Man	0.05-95
Propane	C ₃ H ₈	No symptoms after brief exposure	<10,000	1	Man	12-94
		Odor not detected	<20,000	2	Man	
		No irritation, but slight dizziness in a few minutes	<100,000	10	Man	
Butane	C ₄ H ₁₀	Odor not detected	<5,000	0.5	Man	0.01-182
		No systemic effects except drowsiness	10,000 for 10 mins	1.0	Man	
Pentane	C ₅ H ₁₂	Threshold limit	1,000	0.1	Man	0.023-64
		Odor readily detectable	5,000	0.5	Man	
		No mucous membrane irritation or other symptoms	5,000 for 10 mins	0.5	Man	
		Narcosis in 5 to 60 mins	90,000-120,000	9-12	Mice	
Hexane	C ₆ H ₁₄	Threshold limit	500	0.05	Man	4-27
		No symptoms	2,000 for 10 mins	0.2	Man	
		Dizziness and sensation of giddiness	5,000	0.5	Man	

TABLE 12 (Continued)

Hydrocarbon	Formula	Health Effects	Concentration (ppm)	Percent of Volume of Air	Subject	Ambient Concentrations (ppb)
Hexane (cont'd)	$C_{16}H_{14}$	Narcosis Convulsions and death have resulted from exposures of equal duration	30,000 35,000-40,000	3.0 3.5-4.0	Mice	
Heptane	C_7H_{16}	Threshold limit Slight vertigo	500 5,000 for 6 mins 2,000 for 4 mins	0.05 0.1 0.2	Man Man Man	0.2-34
		Intoxication charac- terized by uncon- trolled hilarity in some individuals and in others a stupor lasting for 30 mins after exposure; these individuals complained of loss of appetite, slight nausea, and a taste resembling gasoline	5,000 for 15 mins	0.5	Man	
		Narcosis	10,000-15,000 for 30-60 mins	1-1.5	Mice	

TABLE 12 (Continued)

Hydrocarbon	Formula	Health Effects	Concentration (ppm)	Percent of Volume of Air	Subject	Ambient Concentrations (ppb)
Heptane (Cont'd)	C ₇ H ₁₆	Convulsions/death	15,000-20,000 for 20-60 mins	1.5-2.0	Mice	
Octane	C ₈ H ₁₈	Threshold limit	500	0.05	Man	0.04-3.4
		Narcosis in 30-90 mins	6,600-13,700	0.66-1.37	Mice	
		No deaths or convulsions	<13,700 for 30-90 mins	1.37	Mice	
Ethylene	C ₂ H ₂	TLV ^b	1,000	0.1	Man	0.7-700
		MPL ^c	5,500	0.55	Man	
Propylene	C ₃ H ₆	MPL ^c	4,000	0.4	Man	1-52
1-Butene	C ₄ H ₈	MPL ^c	1,000	0.1	Man	0.7-700
1,3-Butadiene	C ₄ H ₆	TLV ^b	1,000	0.1	Man	1-9
		Only slight eye and upper respiratory tract irritation in man	8,000 for 8 hrs	0.8	Man	
		No deleterious effects from these exposures; however, the animals were slightly anesthetized, showing a loss of pupillary reflex. Noisy breathing and rales were noted	200,000-250,000 once a day for 15-21 days	20-25	Rabbits	

TABLE 12 (Concluded)

Hydrocarbon	Formula	Health Effects	Concentration (ppm)	Percent of Volume of Air	Subject	Ambient Concentrations (ppb)
2-Methyl-1,3-butadiene (isoprene)	C ₅ H ₈	No narcosis	20,000 for 2 hrs 35,000-40,000	2 3.5-4.0	Mice	0.2-2.9
Acetylene	C ₂ H ₂	MPL ^c Slight intoxicating effect Marked intoxication Incoordination Unconsciousness in 5 mins	5,000 100,000 200,000 300,000 350,000	0.5 10 20 30 35	Man Man Man Man Man	0.2-227

^aConcentrations appearing in the literature up to 1978.

^bTLV - Threshold limit value.

^cMPL - Maximum permissible level.

Source: U.S. Environmental Protection Agency 1980.

TABLE 13

EFFECTS OF ALKANE VAPOR EXPOSURE ON HUMANS

Alkane	Subjects	Exposure Concentration and Duration	Effects
Pentane	3-6 men and women	Up to 5,000 ppm, 10 mins	No symptoms
Hexane	3-6 men and women	5,000 ppm, 10 mins	Marked vertigo, giddiness
Hexane	6 men and women	2,500-1,000 ppm, 10-12 hrs/day	Drowsiness in 0.5 hr, fatigue, loss of ap- petite in some, paresthesia in distal extremities
Hexane	93 men and women	2,500-5,000 ppm (duration un- known)	Sensory impairment in distal portion of ex- tremities, muscle weakness in 13, cold sensation of extremities in some, blurred vision, headache, easy fatiguability, anorexia, weight loss at onset of poly- neuropathy, muscular atrophy, demyelina- tion and axonal degeneration of peripheral nerves
Hexane	3-6 men and women	2,000 ppm, 10 mins	No symptoms
Hexane	3 women	1,300-6,500 ppm, 2-10 months	Headache, burning sensation of face, abdom- inal cramps, numbness, paresthesia, weakness of distal extremities, bilateral foot and wrist drop, absence of Achilles tendon reflexes, fibrillation potentials, decreased conduction time in motor and sensory nerves, denervation-type injury of muscles, numerous neuropathologic changes

TABLE 13 (Concluded)

Alkane	Subjects	Exposure Concentration and Duration	Effects
Hexane	11 men and women	1,000-5,000 ppm, 3-6 months	Fatigue, anorexia, paresthesia in distal extremities, muscular atrophy
Hexane	4 men and women	Exposure data not available	Peripheral neuropathy, reduced motor and sensory nerve conduction velocities, knee- jerk and Achilles tendon reflexes absent, muscular atrophy, diminished sensations of heat and touch, pathologic abnormalities in muscles and nerves
Heptane	3-6 men and women	5,000 ppm, 15 mins	Marked vertigo, lack of coordination, hilarity for 30 mins
Heptane	3-6 men and women	5,000 ppm, 7 mins	Marked vertigo, lack of coordination of space, hilarity in some
Heptane	3-6 men and women	5,000 ppm, 4 mins	Marked vertigo, inability to walk straight, hilarity
Heptane	3-6 men and women	3,500 ppm, 4 mins	Moderate vertigo
Heptane	3-6 men and women	2,000 ppm, 4 mins	Slight vertigo
Heptane	3-6 men and women	1,000 ppm, 6 mins	Slight vertigo
Octane	No data available		

Source: National Institute of Occupational Safety and Health 1977a.

The volatile acyclic and alicyclic hydrocarbons have not been demonstrated as carcinogenic, teratogenic, or mutagenic in humans or animals. However, some of the longer-chain (C_{12} or greater) alkanes have been implicated as co-carcinogens, based on mouse skin experiments.

Acyclic hydrocarbons are generally metabolized to alcohols, which may be further metabolized to ketones, aldehydes, and acids. Alkenes (olefins) may be oxidized at saturated positions to yield alkenols.

Lower-molecular-weight hydrocarbons affect the surface tension and electrical conductivity of lipids, proteins, and lipoprotein membranes. These effects are related to their narcotic effects. In general, branched lower alkane isomers are less active and less toxic than normal (straight chained) alkanes.

Animal experiments, usually with dogs, show definite inhibition of cardiac performance due to propane, butane, and isobutane (Aviado et al. 1977). Effects include a decrease in myocardial contractility, a decrease in mean aortic pressure and stroke work, a decrease in total cardiac output, and an increase in pulmonary vascular resistance. Mean threshold concentrations for these effects are in the 2 to 3 percent (volume/volume) range. Threshold levels vary, depending on other components in the respired air. The cause of these hemodynamic effects is unknown; they may be direct effects on the vascular system or may be induced via central nervous system depression.

Hydrocarbon Neuropathy

Scala (1976) wrote that, "Hydrocarbon Neuropathy is a clinical entity of relatively recent description." Peripheral, chemically-induced neuropathies are believed to result from impairment of metabolism in neuron (nerve) cell bodies. Distant portions of the body's longest axons become poorly nourished and degenerate--with the nerve fiber steadily "dying back" as the disease progresses. The longest sciatic nerves are affected first, with a decrease in sensation and motor abilities, first in the feet, then in the hands. Complete recovery has been claimed when the disease is treated early. Otherwise, permanent sensory and motor deficits result. Reported symptoms include numbness, paresthesia (loss of tactile senses), tenderness, muscle weakness, fatigability, lassitude, constriction of the visual field, muscle atrophy, hypo- and hyperactive reflexes, and pain (Scala 1976). Some patients experience a continuous increase in severity of the symptoms, even after several months of treatment and removal from sources of exposure.

Most clinical reports of hydrocarbon neuropathy involve poorly characterized occupational exposures to n-hexane. A majority of cases involve exposure to technical or solvent grade hexane which may commonly contain significant amounts of other C₅ through C₉ alkanes, cycloalkanes, and aromatic compounds, including benzene and toluene. Technical grade hexane, defined by its physical properties, frequently contains less than 50 percent n-hexane. Hydrocarbon exposure levels on the order of over 500 ppm have caused neuropathy outbreaks. Glue-sniffing cases, involving deliberate inhalation of hexane-containing toluene, have been reported to be clinically different from occupational n-hexane polyneuropathy. It is unknown whether toluene modifies the action of hexane, or if the different mode of exposure (short-term, high concentration) affects disease development.

Limited animal studies have assessed the peripheral neuropathy associated with hydrocarbon exposures (Scala 1976). In general, these studies confirm the occupationally observed polyneuropathies. Peripheral nerve degeneration and sensorimotor deficiencies are observed after chronic, 1- to 6-month exposures to technical grade hexane.)

The hydrocarbon 2-hexanone (methyl-n-butyl ketone) exhibits a polyneuropathy in animals similar to that caused by hexane. Both n-hexane and 2-hexanone have common metabolites, 2,5-hexanedione and 5-hydroxy-3-hexanone. The 2,5-hexanedione has demonstrated neurotoxic effects in animals, but other alkane metabolites require thorough testing. A critical 2- or 2,5-relationship for oxygen-bearing atoms may be associated with neurotoxicity. Similar oxidative metabolic reactions have been demonstrated with heptane. Metabolic reactions of hexane, heptane, and other hydrocarbons to neurotoxic metabolites require investigation. A structurally-based, generic, metabolic cause of hydrocarbon polyneuropathy may be possible and bears examination. As exposure to pure hydrocarbons is rare, studies are needed involving synergistic and other interactive neurotoxic effects among hydrocarbons and other agents commonly found in the workplace.

Alicyclic Hydrocarbons

The toxicological effects of alicyclic hydrocarbons closely resemble those of the acyclic hydrocarbons, however their toxicities do not correlate as well as the acyclics with respect to structure (e.g., number of carbon atoms, degree of unsaturation). There are few reported cases of human exposure to alicyclic hydrocarbons because they are infrequently used or encountered in pure form. Animal toxicity for these compounds is summarized in Table 14.

TABLE 14

TOXICITY OF ALICYCLIC HYDROCARBONS

Hydrocarbon	Formula	Health Effects	Concentration			Exposure		Subject	Type of Study	Ambient Concentrations (ppb)
			(ppm)	(mg/m ³)	(% by Air)	Hrs	Days			
Cyclohexane ^a	C ₆ H ₁₂	No effect	434	1,491	0.043	8	130	Rabbits	Chronic	3-6
		Minor microscopic changes in kidneys and liver	786	2,710	0.078	6	50	Rabbits	Chronic	
		No effect	1,243	4,270	0.12	6	50	Monkey	Chronic	
		No fatalities or signs of injury	3,300	11,439	0.33	6	50	Rabbits	Chronic	
		Some fatalities	7,400	25,419	0.74-1.85	6	10	Rabbits	Chronic	
		No deaths	18,500	63,548	1.85	8	1	Rabbits	Acute	
		Deaths	26,600		2.66	1	0	Rabbits	Acute	
Methylcyclohexane	C ₆ H ₁₁ CH ₃	No effect	241	996	0.024	24	70	Rabbits	Chronic	3-7
		No effect	1,162	4,659	0.116	24	70	Rabbits	Chronic	
		No effect	2,800	11,228	0.28	24	70	Rabbits	Chronic	
		Minor evidence of kidney and liver injury	3,300	13,233	0.33	5	70	Rabbits	Chronic	
		No fatalities								
		lethargy in 50%	5,600	22,456	0.56	6	28	Rabbits	Chronic	

TABLE 14 (Concluded)

Hydrocarbon	Formula	Health Effects	Concentration			Exposure		Subject	Type of Study	Ambient Concentrations (ppb)
			(ppm)	(mg/m ³)	(% by Air)	Hrs	Days			
Methylcyclohexane (Cont'd)		25% fatalities	7,300	29,273	0.73	6	14	Rabbits	Chronic	
		100% fatalities	10,000	40,100	1.0	6	14	Rabbits	Chronic	
		100% fatalities	15,000	60,150	1.5	70 mins	0	Rabbits	Chronic	

^aThe threshold limit value for cyclohexane is 400 ppm.

^bThe threshold limit value for methylcyclohexane is 500 ppm.

Source: U.S. Environmental Protection Agency 1980.

Alicyclics act as general anesthetics and central nervous system depressants with a relatively low order of acute toxicity. Massive acute exposure may cause asphyxiation and narcotic effects--exhilaration, vertigo, headache, anorexia, incoordination, and nausea. Most cycloalkenes such as cyclopentene, cyclohexene, and cycloheptene are known to be metabolized to their corresponding, more toxic trans-diols in in vitro microsomal preparations.

Chronic animal exposure studies are deficient with respect to alicyclic dose-response relationships (U.S. Environmental Protection Agency 1980a). Available occupational and epidemiological studies do not demonstrate systemic effects due to naphthenes. Naphthenes (hydrocarbons with fused six-member nonaromatic rings) are abundant in gasoline and gasoline vapors and behave much like other alicyclics.

Alicyclics tend not to accumulate within the body. Most cycloalkanes are rapidly exhaled, metabolized, and eliminated in the urine as glucouronide and sulfate derivatives.

Aromatic Hydrocarbons

Benzene. Concentrations of benzene vapors over 100 ppm, in either acute or chronic exposures, may cause multiple central nervous system (CNS) and other effects--euphoria, dizziness, confusion, narcosis, CNS stimulation followed by depression with respiratory paralysis, mucous membrane irritation with pulmonary edema, gastrointestinal irritation, skin blistering, and paresthesia (loss of tactile senses). Benzene toxicity is summarized in Table 15. Most acute effects are reversible. Benzene is quite soluble in body fluids and tissues. Due to its high vapor pressure, it is rapidly eliminated via lungs and concentrated in urine by the kidneys within minutes after exposure terminates. It is primarily metabolized to phenol, with minor metabolites including trans-1,2-dihydrobenzene, catechol, hydroquinone, phenylmercaptic acid, and trans-muconic acid. Hydroxylated species are further metabolized and excreted as conjugated glucouronides and sulfates.

Chronic exposure to benzene may elicit a number of responses, including leukemia, pancytopenia, and chromosomal aberrations. Hematopoietic (blood forming) anomalies can affect a number of blood parameters, including erythrocyte count, hemoglobin, mean corpuscular volume of red blood cells, platelet counts, and leukocyte counts. These abnormalities have developed as a result of repeated occupational exposure to benzene concentrations from 60 to 105 ppm. Benzene chronic exposures as low as 20 to 25 ppm have been associated with hematologic alterations (U.S. Environmental Protection Agency 1980).

TABLE 15
TOXICITY OF BENZENE

Health Effects	Concentration			Subject	Type of Study	Ambient Concentrations (ppb)
	(ppm)	(mg/m ³)	(% by Air)			
TLV	25	80	0.0025	Man	Acute	0.025-57
Mucous membrane Irritation	100	319	0.01	Man	Acute	
Threshold for affecting central nervous system	370	1,180	0.037	Mice	Acute	
Endurable for 0.5-1.0 hrs	3,000	9,570	0.3	Man	Acute	
Prostration	4,700	14,993	0.47	Mice	Acute	
LC 50	7,400	23,606	0.74	Mice	Acute	
Dangerous after 0.5-1.0 hrs	7,500	23,925	0.75	Man	Acute	
LC 100	14,100	44,979	1.41	Mice	Acute	
LC 100	17,800	56,782	1.78	Rats	Acute	
Fatal after 5-10 mins	20,000	63,800	2.0	Man	Acute	

Note: TLV = threshold limit value.

LC 50 = lethal concentration 50.

LC 100 = lethal concentration 100.

Source: U.S. Environmental Protection Agency 1980.

Benzene is recognized as a toxic agent. Exposure has caused leukemia in some animal studies. Human occupational exposure experience and epidemiological studies confirm benzene's leukemia-causing potential, but do not support accurate derivation of dose-response curves. Most of these studies report exposure levels of 100 to 500 ppm. Benzene was recently judged to be fetotoxic to rats at exposures of 50 and 500 ppm and to cause teratogenic effects at 500 ppm (Kuna and Kapp 1981). NIOSH recently revised its recommendations for the threshold limit value for occupational exposure to benzene from 10 ppm to 1 ppm; however, the U.S. Supreme Court blocked enforcement of the lower exposure limit.

Toluene and Xylenes. Toluene and xylene isomers are methyl derivatives of benzene (toluene is 1-methylbenzene and xylene is dimethylbenzene). Xylene exists in three isomeric forms determined by the relative position of two methyl groups on the six-member benzene ring: 1,2 (ortho); 1,3 (meta); and 1,4 (para). These two aromatics act as irritants on skin and mucous membranes, including the respiratory tract and conjunctiva (eyes). These compounds were thought to affect the blood, blood-forming organs, and nervous system, much the same as benzene (National Institute for Occupational Safety and Health 1975a). However, recent testing suggests that benzene and other contaminants were primarily responsible for these effects. Acute toxicity tests for these compounds are suspect, unless the agents tested are fully characterized and the amount of benzene is low, on the order of less than 0.1 percent (100 ppm) (National Institute for Occupational Safety and Health 1975a).

The major toxic effects of these compounds (summarized in Table 16) are due to their narcotic properties. Habituation to toluene has occurred in painters and "glue sniffers." These persons may purposefully absorb toluene up to the point of unconsciousness, but in most cases no permanent pathological changes occur. Xylene toxicity is similar, although it may be slightly more irritating. These compounds detrimentally affect human judgment, attention, performance, and perception, but these effects have not been quantified relative to other hydrocarbons.

Toluene is readily metabolized to benzoic acid, which is eliminated as hippuric acid in the urine. Small amounts of benzyl alcohol intermediate may be isolated and lesser amounts of systemic toluene are hydroxylated to o- and p-cresol. Xylene metabolism involves oxidation of a methyl group, conjugation with glycine or glucouronic acid, and excretion as methylhippuric acid. While some xylene may be hydroxylated to phenolic metabolites, the amount is small and apparently does not significantly affect acute toxicity.

TABLE 16
TOXICITY OF TOLUENE AND XYLENES

Hydrocarbon	Formula	Health Effects	Concentration			Exposure		Subject	Type of Study	Ambient Concentrations (ppb)
			(ppm)	(mg./m ³)	(% by Air)	Hrs	Days			
Toluene	C ₆ H ₅ CH ₃	No effect	50-100	188-377	0.05-0.01	---	---	Man	Acute	0.005-129
		Mild fatigue, weakness, confusion, skin paresthesias	200	753	0.02	8	1	Man	---	
		Same symptoms more pronounced	300	1,130	0.03	8	1	Man	---	
		Same symptoms plus mental confusion	400	1,506	0.04	8	1	Man	---	
		Same symptoms plus nausea, headache, dizziness	600	2,259	0.06	3	1	Man	---	
		Same symptoms plus loss of coordination, staggering gait, and dilated pupils	600	2,259	0.06	8	1	Man	---	
		Same symptoms as above with after effects characterized by severe nervousness, muscular fatigue, and insomnia	800	3,012	0.08	8	1	Man	---	

TABLE 16 (Concluded)

Hydrocarbon	Formula	Health Effects	Concentration			Exposure		Subject	Type of Study	Ambient Concentrations (ppb)
			(ppm)	(mg/m ³)	(% by air)	Hrs	Days			
Xylenes (O,M,P)	C ₆ H ₄ (CH ₃) ₂	Threshold for affecting central nervous system	174	755	0.017	---	---	Mice	Acute	2.5-119
		Threshold limit value (TLV)	200	868	0.02	---	---	Man	Acute	
		No hematologic effects	690	2,995	0.069	8	130	Rat and Rabbit	---	
		Decreased leukocytes and red blood cells; increased platelets	1,150	4,991	0.115	8	55	Rabbit	---	
		Prostration	4,699	20,394	0.469	---	---	Mice	Acute	
		LC50	9,200	39,928	0.920	---	---	Mice	Acute	
		LC100	12,650	54,901	1.26	---	---	Mice	Acute	
		LC100	17,250	74,865	1.72	---	---	Rat	Acute	

Note: --- Represents data not available or applicable.

Source: U.S. Environmental Protection Agency 1980.

NIOSH has recommended a time weighted average concentration of 100 ppm and a ceiling limit of 200 ppm for toluene and xylene. These recommendations are primarily based on a lack of data to alter existing standards, rather than on recent, adequate studies of humans or animals.

No epidemiological studies characterizing exposures to these compounds are available, but they are underway at NIOSH. Data concerning the mutagenic, teratogenic, fetotoxic, and carcinogenic properties of these compounds (in pure form) are not available either. Older studies or observations of these and other effects should be evaluated in light of probable contamination by benzene and other compounds. Impurities in these commercial products, when derived from petroleum, may include benzene, toluene (in xylenes), xylenes (in toluene), ethylbenzene, trimethylbenzene, phenol, thiophene, pyridine, and nonaromatic compounds (National Institute for Occupational Safety and Health 1975a). Complex mixtures of benzene and other aromatics are likely to be encountered in refinery process streams. Benzene commonly occurs in gasoline and other fuels (see the End Use section of this report).

Phenolic Compounds. Phenolic compounds--those with an aromatic (benzene) ring to which a hydroxyl (OH-) group is attached--occur in crude oil and its fractions, and in high concentration in acidic petroleum extracts. Phenolic compounds include phenol, cresols, thiophenols, alkyl phenols, and alkyl cresols. They generally are water soluble and exist in refinery solid, liquid, and atmospheric emissions and wastes. Phenolic compounds are acidic and on contact are corrosive to skin, eyes, and membranes. Most are readily absorbed into the body when contact or exposure occurs. Phenolics have been found to act as carcinogens and co-carcinogens in animal testing and to induce a host of cytologic and genetic changes during in vitro testing.

Phenol readily enters the body through a number of routes--including percutaneous absorption, inhalation, and ingestion (National Institute for Occupational Safety and Health 1976). Because of its relatively low volatility and characteristic odor, it does not frequently pose a respiratory hazard at ambient temperatures. Skin and other membranes burn on concentrated contact. Symptoms following exposure may include nausea, vomiting, difficult breathing, pulmonary edema, headache, dizziness, visual disturbances, convulsions, and partial paralysis.

Phenol is readily metabolized and excreted as conjugated glucuronides and sulfates, with some small amounts oxidized to quinone and catechol-related compounds. The average human fatal dose is in

the range of 15 grams, but as little as 1 gram has been reported to cause death, even by skin absorption (Windholz 1976). Chronic exposure may lead to pulmonary and hepatic disorders.

The Occupational Safety and Health Administration has set a time weighted average (TWA) limit of five ppm for continuous occupational skin exposure to phenol. NIOSH has recommended air concentration limits of 20 mg per m³ as a TWA and 60 mg per m³ for any 15-minute exposure.

Phenol has been reported to be carcinogenic and co-carcinogenic in some animal experiments, but is not presumed to be a human carcinogen.

Cresols exist in crude oil and various refinery process and waste streams. Cresols, also known as hydroxy-methylbenzene, methylphenol, and hydroxytoluene, possess a methyl and hydroxyl group attached to a six-member aromatic (benzene) ring. There are three isomeric forms--1,2 (ortho); 1,3 (meta); and 1,4 (para). Cresol isomers are difficult to separate and cresylic acid refers to mixtures of cresols and other phenolic compounds with similar boiling ranges. Cresols are highly reactive--oxidizing to form more toxic quinones and hydroxybenzenes in the atmosphere and in water (Gordon 1976). Their estimated detectable lifetime is 1 day in air and less than 10 days in water. The chemical behavior of cresols is similar to that of phenol--mildly acidic and soluble in water.

Cresols, like phenol, may be absorbed through the skin and mucous membranes, causing severe irritation and corrosive tissue burns when in concentrated form. No data are available concerning the toxicity of cresol vapors to humans, but acute inhalation hazards at ambient temperatures should be low due to their low vapor pressure and characteristic odor, noticeable well below hazardous levels. Cresols especially affect the central nervous system, liver, and kidneys (Gordon 1976). Cresols have long been used commercially for their microbicidal effects.

Cresols are commercially produced within some refineries from acid extracted phenolic fractions after thermal or catalytic cracking (Gordon 1976). These solutions may contain 25 percent phenols, cresols, and xlenols. Cresols may also be present in phenolic liquid wastes and air emissions.

A U.S. time weighted average of 5 ppm (22 mg per m³) in the air based on a 40-hour work week exposure has been set. However, the Federal Republic of Germany (West Germany) has established a more stringent standard of 0.05 ppm for a 30-minute averaging period and a permissible standard (i.e., not to exceed more than once in any 4-hour period) of 0.15 ppm.

p-cresol exists in a number of natural products and is permitted as a food and cosmetic additive in the U.S. However, the Council of Europe has classed p-cresol as an "artificial flavoring substance not admissible at present" (Gordon 1976).

Cresols, like phenol, have been ascribed with tumor-promoting, co-carcinogenic properties. Several animal studies with cresol-containing extracts of natural products have reported significant co-carcinogenicity. Teratogenic effects of the central nervous system have been reported for rats orally administered 0.0001 mg per kg of p-cresol per day for 8 months.

Sulfur Compounds

Hydrogen Sulfide. Hydrogen sulfide (H_2S) is a leading cause of death in the workplace (National Institute for Occupational Safety and Health 1976). Substantial quantities are extracted and produced in petroleum refineries, which usually convert it to sulfur or burn it in flares. Most reports of human H_2S toxicity involve acute occupational exposures.

Acute exposure to high concentrations, usually over 1,000 ppm, produces unconsciousness immediately and death in several minutes due to respiratory paralysis. At lower concentrations (200 ppm or less), hydrogen sulfide may cause eye irritation; conjunctivitis; blurred vision; and corneal blistering, opacity, and pitting. The presence of carbon disulfide accelerates development of these symptoms. The symptoms usually subside within several days, but secondary bacterial infection may cause permanent injury.

Olfactory thresholds for hydrogen sulfide exhibit both dose-response and duration-response relationships. The lower limit for H_2S odor detection is 0.02 to 0.03 ppm. At concentrations up to 30 ppm it has an odor of rotten eggs, while above 30 ppm it may seem sweet or sickeningly sweet. Above about 100 ppm, hydrogen sulfide may not be detectable due to olfactory fatigue, which may result from prolonged exposure to lower concentrations. Thus, odor cannot be relied upon as a warning of dangerous H_2S concentrations. Headaches are a common result of exposure to low concentrations of H_2S .

There are few reports of humans suffering permanent adverse effects from long-term exposure to H_2S below 50 ppm. Few chronic low-level animal studies have been performed. NIOSH has recommended a ceiling limit of 10 ppm (15 mg per m^3) for continuous occupational exposure, and a limit of 50 ppm (70 mg per m^3) for short-term exposures (National Institute for Occupational Safety and

Health 1977b). No literature reports link H_2S human airborne exposures with carcinogenic, mutagenic, or teratogenic effects. Chronic exposure to H_2S and carbon disulfide combinations have caused weak teratogenic effects in rats. No information is available concerning the extent of low-level chronic and acute exposures among refinery workers and persons in the neighborhood of refineries.

Hydrogen sulfide is heavier than air and may accumulate to toxic levels in confined spaces, pits, sewers, and low areas. H_2S has upper and lower explosive limits of 4.3 percent and 45.5 percent, respectively. Federal regulations require precautions to ensure levels below 0.43 percent (4,300 ppm), or 10 percent of the lower explosive limit. Because H_2S readily causes corrosion and brittleness in metal piping and fittings, these require frequent inspection, monitoring, and maintenance. Extensive monitoring and alarm devices, employee training, and respiratory equipment are required wherever H_2S may be encountered in the workplace.

Available epidemiological studies suggest that certain individuals may be particularly susceptible to H_2S at low levels. Eye and pulmonary irritation, nausea, abdominal cramps, headaches, acute asthma attacks, and sleep disturbances were observed in the general population exposed to less than 0.125 ppm in a 1964 air pollution incident in Terra Haute, Indiana. A particular hazard may exist for susceptible individuals such as the aged, infants, infirm, and those with lung or heart ailments. Such sensitive persons are not likely to remain employed in H_2S exposure-prone refinery operations.

Thiol Compounds. The terms thiol, mercapto, and sulfhydryl may be used interchangeably, with thiol being the preferred term for the -SH group, the sulfur-containing analog of the hydroxyl group that characterizes alcohols. Thiols may constitute several percent by weight of crude oils, especially sour and heavy crude oils. Thiol compounds present in crude oil include the alkyl thiols with a thiol group attached to the primary carbon, such as 1-butanethiol, and cyclic thiols, primarily cyclopentanethiol and cyclohexanethiol.

Thiols are highly objectionable in refined petroleum products. Their acidity corrodes most metal alloys, they contribute to the total sulfur content of fuels, and they cause significant odor problems. Sweetening processes using oxidants, such as sodium plumbite or cupric chloride, convert thiols into non-corrosive, less malodorous disulfides. Thiols are removed by extraction with amine and other caustic solutions, and by hydrotreating.

Naturally occurring thiols exist in nearly all living systems. Examples are cysteine, an amino acid, and glutathione. Thiols and disulfides are involved in many of the body's natural metabolic processes.

The C₁ through C₅ alkane thiols have relatively high vapor pressures and obnoxious odors at low concentrations. Higher alkane thiols, cyclohexanethiol, and benzenethiol have relatively lower vapor pressures, and thus are less volatile. Methanethiol is a gas at room temperature, and the others are liquids. Thiols are relatively insoluble in water, act as weak acids, and form insoluble mercaptides with a variety of metal cations found in petroleum, including lead, copper, cadmium, silver, and mercury.

Odor intensity thresholds for several thiols are presented in the End Use section of this report. Because of their low thresholds--as low as 0.02 ppb--alkane (C₁ through C₃) thiols are commonly used as natural gas odorants to warn of gas leakage. Methanethiol is a major contributor to abnormal mouth odor. The odor of onions is primarily due to 1-propanethiol, and butanethiol is a major odorant in skunk secretions. Nausea is the most common response to strong thiol odors.

Thiols exert their primary toxic effect on the central nervous system (National Institute for Occupational Safety and Health 1978). Acute exposure to high concentrations (over 50 ppm) in humans and animals may cause narcosis, cyanosis, paralysis, fatigue, coma, and death from respiratory failure. The alkane C₁ through C₆ thiols are relatively equitoxic when inhaled, and less toxic than heavier thiols. Definitive studies to determine thiols' dose-response and structure-activity relationships are lacking. Most available human toxicity data are derived from odor threshold studies. Thiols' toxic effects may be additive upon simultaneous exposure.

Animal experiments and human observations suggest that the compounds exert ocular and cutaneous effects (National Institute for Occupational Safety and Health 1978). Animal experiments show that the higher (longer chain) alkane thiols may cause contact sensitization. Octadecanethiol, applied undiluted to mouse skin, produces hyperplasia of the follicles, sebaceous gland degeneration, hyperkeratinization, a decrease in skin delta-7-cholesterol, and an increase in skin cholesterol. These changes are similar to those resulting from dermal application of methylcholanthrene, a known skin carcinogen. Studies are not available which determine whether similar effects occur in humans. Because of their acidic nature, thiols cause eye irritation. Human ocular effects are not well documented or studied and neither are human acute or subchronic dermal effects.

No data on reproductive or teratogenic effects of thiols are available. Several studies suggest a potential human mutagenic effect, but these studies involved simultaneous exposure to chloroprene, a known mutagen. Carcinogenic effects have not been investigated.

NIOSH has recommended a threshold limit value (TLV) of 0.5 ppm in air for exposure to any combination of thiols for any 15-minute period. As permanent effects from low-level exposures have not been documented, no time weighted average or ambient workplace concentrations have been recommended. Because benzenethiol is more toxic and irritating, a TLV of 0.1 ppm (0.45 mg per m²) has been recommended.

No epidemiological studies concerning thiols are available, nor is there any information concerning thiol exposures within petroleum refineries and their environs.

Nitrogen Compounds--Health Effects

Ammonia. Ammonia (NH₃) is a colorless gas that acts as a base in water or biological fluids, forming ammonium hydroxide (NH₄OH). It has a characteristic odor which is detectable and recognizable above approximately 1 ppm. Caustic ammonia solutions are used in refineries for scrubbing crude fractions to remove acidic compounds, primarily thiols and phenolics. Ammonia is also still in limited use as a refrigerant, although it is being phased out.

Available human studies and clinical reports do not fully elaborate on dose-responses for ammonia exposures (National Institute for Occupational Safety and Health 1974). In low concentrations (less than several hundred ppm), ammonia atmospheric exposure causes upper respiratory irritation and eye irritation. Low concentrations generally do not reach the lower lungs. Solutions of 1 to 3 percent ammonia cause skin irritation and may cause blistering on prolonged contact. At high concentrations, ammonia vapors may cause pulmonary edema, suffocation, and permanent damage (burns) to the skin, mucous membranes, and cornea.

Systematic epidemiological studies of ammonia exposures are not available. Several studies indicate a possible excess of cancer deaths in workers exposed to moderate ammonia levels (National Institute for Occupational Safety and Health 1974). Animal studies indicate that inhalation of ammonia in concentrations as low as 100 ppm decreases ciliary activity. Available animal and human studies indicate no permanent health hazards from intermittent, low-level ammonia exposures. Plant surveys indicate that concentrations in the range of 5 to 50 ppm may cause eye and respiratory irritation in some individuals. Animal studies indicate that airborne particulates may potentiate ammonia's toxic effects, apparently by facilitating ammonia transport deeper into the respiratory tract. In animal studies, tracheal damage was found to increase with ammonia adsorbed on inhaled carbon particles.

NIOSH has proposed a ceiling limit of 50 ppm for any occupational exposure to ammonia vapors. Some persons may find this level disagreeable, but no permanent injuries can be expected from this or other brief exposures to less than several hundred ppm. These values are well below the annoyance odor threshold for ammonia.

Theoretical modeling and accident reports indicate that extremely hazardous ammonia concentrations can exist at considerable distances downwind from liquid anhydrous ammonia spills. In one test, one ton of liquid (compressed) anhydrous ammonia was spilled into a pool and 50- to 1,000-ppm concentrations were measured downwind. Modeling indicates that the sudden release of 1,000 tons of anhydrous ammonia from a pressurized storage tank could result in fatal exposures 3.2 or more miles (5 kilometers) away (Fryer et al. 1979). Ammonia is ignited with difficulty, although its ignition temperature is lowered in a mixture with oil and in the presence of iron.

No studies of ammonia's teratogenic or carcinogenic effects are available.

Nitrosamines in Refineries. Nitrosamines are substances having an N-nitroso group (nitrosyl radical or nitric oxide attached to the nitrogen atom of an amine molecule). Frequently, the amine is a simple alkyl or aromatic hydrocarbon derivative. They are most commonly prepared in the laboratory by the reaction of amines with nitrous acid (HNO_3). Nitrosamines are photosensitive--the nitrosyl group tending to split off on exposure to UV light, and to a lesser extent, on exposure to visible light. The N-nitroso group and its characteristics offer the only common features among nitrosamines and their chemical and physical properties such as volatility and solubility.

The chemistry of nitrosamine formation is not fully understood. However, petroleum refining processes, their air emissions, and ambient polluted atmospheres may individually and together be expected to foster nitrosamine formation. Large quantities of amines--including dimethylamine, ethanolamine, methanolamine, diethanolamine, and diethylamine--are used in petroleum refining for alkaline scrubbing, sweetening, and solvent extraction.

Secondary and atmospheric formation of nitrosamines is a well documented phenomenon. Amines, usually secondary amines, may form nitrosamines through reaction with nitrites, nitrates, or NO_x gases. Nitrogen dioxide (NO_2) and nitric oxide (NO) are refinery emissions, both from combustion and from refinery processing. Crude

oil may contain up to 0.5 percent organic nitrogen compounds. From 20 to 100 percent of this nitrogen may be oxidized during combustion to form nitric oxide and nitrogen dioxide. NO emissions may be oxidized to NO₂ in hot stack gases or through reaction with ozone.

Although data concerning nitrosamine levels within process streams and in the atmosphere around petroleum refineries are largely lacking, conditions there should favor nitrosamine formation. Reactive amines and nitrogen oxides are present in relatively large quantities. A number of other precursors and nitrosating agents may be present:

- o Nitric acid. Nitric acid may be used or formed during processing. Some refineries manufacture nitric acid as a by-product.
- o Bacterial decomposition products. Ammonia, nitrates, and amines may be formed during secondary wastewater treatment or in solid wastes.
- o Incineration by-products. Incomplete incineration of solid wastes may release amines, ammonia, nitrogen oxides, and nitrates.
- o Nitrilotriacetic acid (NTA). NTA may be formed by the reaction of formaldehyde, ammonia, and hydrogen cyanide--all present in refinery process and waste streams and emissions. NTA is a potent chelating agent that has been used as a scale preventative in cooling water systems. The extent of NTA use in refineries for this purpose or as a chelating agent for crude desalting or wastewater treatment is not known. NTA has been found to be carcinogenic in experimental animals.
- o Nitrosamine additives. Nitrosamines have been patented for use as gasoline and lubricant additives. The extent of their use is not known.

Nitrosamine formation is known to be catalyzed by a number of agents that are present in the refinery. Formaldehyde catalysis of alkaline nitrosation appears to be a general reaction of unhindered secondary amines (Roller and Kcefer 1975). Carbonyl compounds, especially aldehydes, can catalyze nitrosation in alkaline or neutral media. Acidic conditions foster some nitrosation reactions.

Nucleophilic anions, such as chloride, acetate, and thiocyanate, are catalysts below pH 3 (Schweinsberg 1975). Some metals may also catalyze nitrosation reactions. These compounds are present in refining process and waste streams.

It is possible that nitrosamines are cycled within the atmosphere. Nitrosamines generally degrade to their precursors on exposure to ultraviolet and visible light. Daylight half-lives on the order of an hour have been observed experimentally. Nitrosamines in the atmosphere may cyclically form at night and degrade during the day. General atmospheric transport and buildup of nitrosamines are not expected due to their photolability. However, diethylnitrosamine formation has been shown experimentally to be accelerated upon exposure of diethylamine to ambient nitrogen oxides levels and sunlight (Grosjean et al. 1977). Such nitrosamines are formed in a photo-oxidative reaction similar to that of smog formation.

Most investigated nitrosation reaction mechanisms involve the presence of water. Atmospheric nitrosamine production may utilize water vapor adsorbed on particulates. Nitrosamine levels in refinery wastewaters have not been thoroughly documented. Nitrosamines may form there from the reaction of amines with nitric acid and other nitrosating agents. Similarly, nitrosamine levels in process streams have not been documented. Some oil- and water-borne nitrosamines may volatilize to the atmosphere. Concentrations of nitrosamines condensed on surfaces in refineries remain unknown.

Many factors that contribute to secondary nitrosamine formation are present in the polluted atmospheres associated with large cities and industrial areas. The presence of petroleum refineries in these areas with their emissions of potential precursors and catalyzing agents may significantly impact local nitrosamine formation.

Nitrosamines are known to be hepatotoxic and carcinogenic. The potency of various nitrosamines in causing acute injury, and even death, has been shown to vary considerably (Walker 1976). Most of the approximately 200 nitroso compounds that have been tested in animal studies have been shown to be carcinogenic. They are versatile carcinogens--inducing many types of organ tumors in nearly all species tested, including primates. Most animal testing has involved oral administration, with small daily doses over an extended period proving more effective than single large doses. Nitrosamines have been reported to exhibit synergistic or additive effects in combination with other carcinogens, including PAHs. Nitrosamines are not mutagenic in most in vitro test systems. Metabolic activation is evidently required for expression of their mutagenic and carcinogenic effects.

Epidemiological studies among workers exposed to nitrosamines suggest these compounds pose a hazard to man. Additional evidence of the carcinogenicity of ingested nitrites, nitrates, nitrosamine-containing foods, and of cigarette smoking (which involves inhalation

of NO_x and amines) implies their carcinogenic potential in man. The limited animal inhalation studies that have been performed suggest that nitrosamines are effective carcinogens when inhaled. The risk to refinery workers, other occupational groups, and the general population from refinery nitrosamines has not been assessed.

Metals

Metals in Oils. Crude oil, refinery intermediates, products, and wastes contain varying amounts of numerous metals. The metals content of crude oils and approximate throughput per year are shown in Table 17. Many metals are essential nutrients, but several (sometimes these same metals) pose carcinogenic, mutagenic, teratogenic, or other toxic hazards. The toxic potential of metals is determined by a number of factors, including oxidation state, route of exposure, concentration, other substances consistent with exposure, frequency of exposure, and physical state.

Metal concentrations in crude oils can range from 1 to 10,000 ppm. Vanadium and nickel are usually the most predominant, and their concentrations generally increase with the asphaltic content or weight of the crude oil--with lighter oils containing less metal (Smith et al. 1975). Most metal atoms are chelated within large hydrocarbon complexes. Refineries treat crude oils by acid extraction and fractionation to reduce metal content prior to catalyst treatments. Little is known about the chemical structure of metallic compounds in crude oils, other than vanadium and nickel. Besides these two metals, cobalt, iron, chromium, arsenic, mercury, zinc, copper, and antimony compounds are likely to be present.

Many metals are undesirable in refining crude to intermediates and final products. Metals act as catalyst poisons (deactivators), causing buildups in internal combustion engines, boilers, and furnaces, and causing miscellaneous undesirable qualities in final products. Refining tends to concentrate about 90 percent of the crude oil's metals content in the heavy distillate residuals, such as residual fuel oils and asphalts, and the liquid and solid waste streams.

Besides metals occurring naturally in crude oil, a variety of metallic substances are employed in refinery operations, notably catalysts and final product additives (e.g., lead compounds in gasoline). Corrosion of steel and other alloys used in refinery piping and equipment adds to the metal content of oil fractions and wastes. Re-refining of used petroleum products, especially lubricants, compounds the metal-associated health and environmental problems from refineries, as discussed in the End Use section of this report.

TABLE 17

METAL CONTENT IN CRUDE OILS

Metal	Concentration Range (ppm)	Average Concentration (ppm)	Tons/Year (calculated from previous column)
Antimony	0.030-0.107	0.055 ± 0.003	31
Arsenic	0.046-1.11	0.263 ± 0.007	148
Barium	Small amounts in Texas crudes	---	---
Cadmium	---	0.03	17
Chromium	0.0016-0.017	0.008 ± 0.003	4.8
Cobalt	0.032-12.751	1.71 ± 0.11	963
Copper	0.13-6.33	1.32 ± 0.01	743
Iron	3.365-120.84	40.67 ± 2.48	22,900
Lead	0.17-0.31	0.24	135
Manganese	0.63-2.54	1.17 ± 0.04	659
Mercury	0.023-30	3.24 ± 0.01	1,820
Molybdenum	0.008-0.053	0.031	17
Nickel	49.1-344.5	165.8 ± 7.1	93,400
Selenium	0.026-1.396	0.53 ± 0.044	300
Silver	Traces in many crudes	---	---
Tin	Identified in Mexican crudes	---	---
Vanadium	4.0-298.5	88.55 ± 0.42	49,900
Zinc	3.571-85.80	29.80 ± 1.27	16,800
Total			187,837.8

Note: ---Represents data not available or applicable.

Source: Smith et al. 1975; Yen 1975.

Lubricants constitute a major source for entry of metals into the environment and metal compounds exposures within the refinery. Metal salts and compounds are added to refined lubricating oils to perform a variety of functions--prolonging a lubricant's usable life, reducing wear, and acting as detergents, bactericides, antistatic agents, and rust inhibitors. Table 18 presents some representative lubricant metallic additives and their uses. The acute and chronic hazards these additives pose to refinery and other workers who come into contact with them are largely unknown. Many are highly toxic and some, such as the dithiocarbamates and chromium salts, may have carcinogenic properties. The constitution and amounts of additives used in various lubricants and petroleum products are unknown; this information is usually proprietary and additive product mixtures are likely to be custom-blended.

Effects of Metals. The concentrations of metals found in refinery intermediates and wastes are unlikely to cause acute toxic effects in humans, but may present chronic health and environmental hazards. Understanding of metals toxicity and adverse effects is confounded by potential synergistic and antagonistic effects among and between various other metals, other substances, and environmental factors such as temperature and pH. Metal compounds may potentiate the toxicity of other compounds. Interreactions between metals and environmental factors are especially evident in aquatic systems, but are also observed in vivo, in the soil, and in the atmosphere.

Metals considered by many to be essential nutrients to higher animals include: chromium, cobalt, copper, iron, manganese, molybdenum, selenium, vanadium, and zinc (Beliles 1975). More limited documentation indicates that several additional metals may be essential: arsenic, barium, cadmium, nickel, and strontium (Smith et al. 1975). However, chronic exposure to compounds containing some of these same metals, such as cadmium, arsenic, lead, selenium, antimony, and nickel compounds, has been strongly associated with carcinogenic effects in humans and experimental animals. Physiological, toxic, and environmental effects of metals found in petroleum are shown in Table 19 (Smith et al. 1975).

In order to understand environmental hazards associated with trace metals, it is necessary to consider where they enter the environment, their transport and transformation, and the means by and forms in which they move through the food chain. However, these factors are poorly understood.

Metals in Refining Wastes. Elemental metals applied to land (e.g., landfarming) are relatively immobile. Metal salts and compounds may be relatively water-soluble and mobile. Many physical-chemical processes affect the mobility of metal compounds, but the

TABLE 18

SOME METALLIC LUBRICANT ADDITIVES AND THEIR USES

Metal	Representative Compounds	Purpose
Antimony	Sb dialkyl dithiocarbamates	Antiwear, extreme pressure, and antioxidant additives in conventional and low-ash-type automotive crankcase oils, industrial and automotive gear oils, greases (amounts $\leq 1-3\%$)
Barium	Ba diorgano dithiophosphates Ba petroleum sulfonates Ba phenolates Ba phosphonates or thiophosphonates	Corrosion inhibitors, detergents, rust inhibitors, automatic transmission fluids, greases
Boron	Borax, boric acid esters	Antiwear agents, antioxidant, deodorant cutting oils, greases, brake fluid
Cadmium	Cd dithiophosphates	Steam turbine oils
Chromium	Cr salts	Grease additive
Lead	Pb naphthenate	Extreme pressure additive, greases, gear oils
Mercury	Organic mercury compounds	Bactericide, e.g., cutting oil emulsions
Molybdenum	MoS ₂ -Mo dibutyl dithiocarbamate and phosphate	Greases, extreme pressure additives
Nickel	Cyclopentadienylnickel complexes	Antiwear agents, minimize carbon deposits, improve lubrication and combustion
Selenium	Selenides	Oxidation and bearing corrosion inhibitors
Tin	Organotin compounds	Antiscuffing additive, metal deactivators
Zinc	Zn diorgano dithiophosphates Zn dithiocarbamates Zn phenolates	Antioxidant, corrosion inhibitors, antiwear additives, detergent, extreme pressure additives, in crankcase oils, hypoid gear lubricants, greases, aircraft piston-engine oils, turbine oils, automatic transmission fluids, railroad diesel engine oils, differential and wet brake lubricants

Source: Smith et al. 1975.

TABLE 19

PHYSIOLOGICAL EFFECTS OF METALS FOUND IN PETROLEUM PRODUCTS

Metal	Human Effects	Animal Effects	Plant Effects	Toxicity Data
Antimony	Dermatitis, keratitis, conjunctivitis, and nasal septum ulceration by contact fumes or dust.	Shortens lifespan when fed to rats and mice. Sb oxide caused pneumonitis and heart and liver damage.	---	≥ 0.1 g lethal oral dose in humans.
Arsenic	Dermatitis, bronchitis, skin cancer. Damages the heart, kidney, nerves, and possibly the liver. GI symptoms in acute systemic poisoning.	Counteracts the toxic effects of Se in rats and chickens. As(V) is nontoxic. Morphol. changes in blood; kidney damage.	0.1 ppm AsO ₂ reduces heterotrophic activity of freshwater micro-flora.	Normal ingestion 0.1 mg/day. Toxic level 5-50 mg/day. Smallest fatal dose recorded 130 mg.
Barium	Baritosis, a benign pneumoconiosis. Soluble salts highly toxic orally. Soluble salts are skin and mucous membrane irritants.	Full strength Ba lubricant dispersant is a mild eye irritant. BaO and BaCO ₃ caused paralysis.	Poisonous to most plants. 0.1 ppm Ba ²⁺ reduces heterotrophic activity of freshwater micro-flora.	LD50 diesel exhaust solids >10 g/kg (animals). LD50 (oral) Ba sulfonates, 3-10 g/kg. Fatal dose in humans ≥ 0.55 g BaCl ₂ .

TABLE 19 (Continued)

Metal	Human Effects	Animal Effects	Plant Effects	Toxicity Data
Boron	Therapeutic use of H_3BO_3 and borax has caused fatalities. CNS depressant and GI irritant. Boranes highly toxic. Cumulative poison.	2,500 mg/liter in drinking water inhibited animal growth.	0.5-1.0 ppm in soil required for growth of fruit trees. 2.0 ppm possibly toxic. Prevents pitting of apples. Most B fertilizer used on alfalfa.	H_3BO_3 fatal dose in adults 15-20 g and in infants 5-6 g.
Cadmium	Cumulative poison. Pulmonary emphysema, hypertension, kidney damage. Cardiovascular disease. Interferes with Zn and Cu metabolism. Inhalation of 0.03-35 mg/m ³ significantly reduced children's weight. GI symptoms.	1 ppm present in many plant and animal tissues. Caries, anemia, and retarded growth in rat. Maximum concentration in earthworms near a highway, 115 ppm.	Stunts growth of lettuce, radish, bean and turnip plants. Tomatoes, barley and cabbage more tolerant. Leaves accumulate excessive amounts when solutions contain a few tenths µg/ml.	LD (oral) for rabbits 200-600 mg. LD50 CdO fume 500 mg/m ³ for rats to 1,500 mg/m ³ for monkeys.
Chromium	Dermatitis, ulceration of skin, perforation of nasal septum, chronic catarrh, emphysema, carcinogenesis when inhaled. Cr(VI) extremely toxic. Not cumulative. Apparently essential in glucose metabolism.	100 ppm recommended limit for fisheries.	5 ppm recommended limit for irrigation water. Soils contg. 0.2-0.4% Cr are infertile. Toxic to some aerobic microbes at ppb level. A micronutrient.	Normal ingestion 0.05 mg/day. Toxic level 200 mg/day. No ill effects from well water with 1.0-25.0 mg/liter. LD (oral) K chromate in rabbits 1.9 g within 2 hrs.

TABLE 19 (Continued)

Metal	Human Effects	Animal Effects	Plant Effects	Toxicity Data
Cobalt	Coitrogenic, lung effects disputed. Dermatitis. No injury from $\text{Co}_2(\text{CO})_8$. Affects heart and GI tract. ~7 mg/day beneficial. Liver and kidney damage.	Essential nutrient. Polycythemia. Bone hyperplasia. Metaplasia in spleen, liver and kidneys. Hyperglycemia due to reversible pancreatic damage.	Essentiality not established.	Normal ingestion 0.002 mg/day; toxic level 500 mg/day. Co metal dust more toxic than salts in lung irritation; lethal dose of either relatively high. LD $\text{Co}_2(\text{CO})_8$ in animals by inhalation 100 ppm.
Copper	Antagonistic to Zn toxicity. Not cumulative. Require 1-2 mg/day. Inhalation of Cu-contg. dust causes lung and GI disturbances. Affects erythrocytes and liver. Skin and mucous membrane irritants.	Ingestion or inhalation caused hemochromatosis and lung and liver injury. Limits: irrigation water, salt-water organisms, and freshwater organisms, 0.1, 0.05 and 0.02 ppm respectively.	A micronutrient. Toxic to some aerobic microbes at ppb level. 0.05 M Cu^{2+} inhibits root growth and 0.1 M stops germination of lettuce.	Normal ingestion 2-5 mg/day; 65-130 mg CuSO_4 dangerous and 648-972 mg highly toxic. 27 g CuSO_4 fatal.

TABLE 19 (Continued)

Metal	Human Effects	Animal Effects	Plant Effects	Toxicity Data
Iron	Siderosis (a pneumoconiosis due to Fe inhalation).	---	A micronutrient.	---
Lead	Brain damage, convulsions, behavioral disorders, death.	Pb naphthenate kills rabbits by skin absorption (death due to pneumonia). Cumulative poison in vertebrates. Renal and vascular poison.	0.1 ppm Pb^{2+} reduces heterotrophic activity in microflora.	Oral toxicity of Pb naphthenate 3.5-5.1 g/kg. Normal Pb ingestion 0.4 mg/day.
Manganese	Chronic Mn poisoning and/or Mn pneumonitis. Reduces Fe absorption. Requirement 3-9 mg/day. Primarily a nerve toxin. CNS symptoms often result in permanent disability.	Pathological effects on nerve cells and the liver. 1.9-9.9 mg is thyroid inhibitor in rats.	A key role in photosynthesis.	
Mercury	Nerve damage and death.	Detrimental to aquatic ecosystems at 0.005 ppm.	0.1 ppm Hg^{2+} reduces heterotrophic activity of microflora.	Normal ingestion 0.005-0.2 mg/day; toxic level 10 mg/day.

TABLE 19 (Continued)

Metal	Human Effects	Animal Effects	Plant Effects	Toxicity Data
Molybdenum	No indication of even an industrial hazard. Not cumulative.	Appears to have a reciprocal antagonism with Cu. Requirement in rats <0.5 mg/day. Low order of toxicity. No fatalities from molybdenic oxide fumes for 25 one-hour exposures at 1.5 mg/ft ³ air. Toxic to ruminants when fed in excess.	Essential to higher plants. Possible role in photosynthesis.	Ingestion of <500 mg/day MoS ₂ non-toxic to animals. 8.1 mg MoS ₂ /ft ³ nontoxic to guinea pigs. MoO ₃ at 5.8 mg/ft ³ very irritating with high mortality. MoO ₃ dust more toxic than fume.
Nickel	Rarely gives systemic toxic effects even from therapeutic doses (65-195 mg NiSO ₄ and 324-454 mg NiBr ₂). Dermatitis, respiratory disorder, carcinogenesis (nose and lung).	Moderately toxic to aquatic organisms. Maximum Ni concentration in earthworms near a highway 38 ppm. Inhibits enzyme systems. Kidney damage (calf). 1-3 mg/kg Ni compound causes intestinal disorders, convulsions, and asphyxia in dogs.	Can be very toxic depending on its chemical form. A micronutrient. 0.01 ppm reduces the heterotrophic activity of freshwater microflora.	Normal ingestion 0.3-0.5 mg/day. 30-73 mg NiSO ₄ 6H ₂ O toxic in humans.

TABLE 19 (Continued)

Metal	Human Effects	Animal Effects	Plant Effects	Toxicity Data
Selenium	May cause caries. Prevents teratogenic effects of Cd and As. Affects kidneys, liver, marrow, and CNS. Se compounds are potent skin and mucous membrane irritants.	Carcinogenic in large doses in rats. Essential to mammals and chicks in low doses. Teratogenic in chicks. "Blind staggers" and "alkali disease" in cattle and "white muscle disease" in sheep.	2.5 mg/liter Se inhibits the BOD and growth of aquatic saprophytic microflora.	Industrial selenosis symptoms when Se in air <0.2 ppm. Liver damage in humans from 5-7 mg/liter in food. Liver cancer in animals from food containing 10 ppm Se. H_2Se and SeO_2 more toxic than S analogs. LD by inhalation of SeO_2 10 ppm for 2 hrs. Normal ingestion 0.2 mg/day; toxic level 5 mg/day. Extreme tolerance limit in food (dry weight) 20 ppm.
Silver	Argyria (impregnation of the tissues with Ag) following absorption from the GI tract or lung. IV injections of colloidal Ag fatal.	Affects immunological capacity. Histopathological changes in tissues of encephalon and medulla of rabbits.	0.0001 ppm Ag^+ reduces the heterotrophic activity of microflora.	

TABLE 19 (Continued)

Metal	Human Effects	Animal Effects	Plant Effects	Toxicity Data
Tin	Little absorbed when ingested. Affects GI tract and CNS. Sn oxide dust produces benign pneumoconiosis. Ingestion of organotin compounds causes acute cerebral edema and often death.	Decreases longevity slightly when fed to rats and mice for life.	Toxic to some aerobic microbes at ppb levels.	500 mg/kg/day of SnCl_2 for 14 months paralyzed a dog. LD50 (IV) R_2SnCl_2 (where R = $\leq \text{C}_8$ alkyl) 5-40 mg/kg rats. Trialkyltin salts are more toxic.
Vanadium	Cardiovascular disease, carcinogenesis. Main toxic effects on respiratory system. V_2O_5 residues from fuels irritating to those who clean oil-fired burners, renew firebrick linings, and clean heat-exchanger tubs (dusts contain 6-20% V).	Feeding 5 mg/liter V^{4+} for life to rats gave no significant reduction in growth or longevity. Not carcinogenic in rats or mice.	Essential for green algae. Stimulates higher green plants in small amounts.	10 mg/kg fatal to rat. Sublethal doses 92-368 ppm. 49 $\mu\text{g}/\text{ml}$ drinking water highly toxic. 0.205 mg/liter causes lung changes in animals. LD (IV) in humans 30 mg V_2O_5 as tetra-vanadate.

TABLE 19 (Concluded)

Metal	Human Effects	Animal Effects	Plant Effects	Toxicity Data
Zinc	Dermatitis, hypertension, arteriosclerotic and heart diseases. 675-2,280 mg/liter is emetic. Causes mineral loss from bones. Most Zn compounds not particularly toxic at moderate concentrations orally. Zn inhibits the teratogenic, embryocidal, and neo-plastic effects of Cd. Essential.	Zn dithiophosphates are severe eye irritants. 0.1-1.0 ppm lethal to fish and other aquatic animals.	Essential. 0.1 ppm Zn^{2+} reduces heterotrophic activity of microflora.	LD50 (oral) Zn dithiophosphates 2.13-3.7 g/kg. LD50 (skin) 11.3 g/kg for rabbits (24-hr contact). Mixed Mg-Zn phenolate LD50 (oral) 9.5 mg/kg. LD50 (oral) $ZnCl_2$ in guinea pigs, rats, and mice 200-350 mg/kg. Normal ingestion Zn 10-15 mg/day.

Notes: LD50 = The dose at which 50 percent of the subject animals die.

CNS = Central nervous system.

--- Represents data not available or applicable.

Source: Yen 1975.

most important factor is the strength of the complexes and chelates they form with soil components. Accumulation of metals by plants grown in contaminated soils depends on soil conditions and plant variety. Some metals may be concentrated by plants, posing serious animal and human health hazards. An example is selenium.

Metals in surface and groundwaters pose largely unknown hazards. Water quality criteria and standards for the metals content of drinking water have been set, but many of these standards are based on inadequate scientific knowledge. Most metals in surface water eventually become physically associated with particles or form organic complexes. They may settle out and become immobilized in sediment. However, some compounds, depending primarily on solubility, particle size, and chemical equilibria, will always be available to enter the aqueous phase, and waters may be contaminated, especially when sediments are disturbed. Aquatic plants, especially algae, are excellent scavengers and concentrators of many metals in surface waters. These plants form the base of higher organisms' food chains and may ultimately be a source for human exposures.

The final fate of the metals content in crude petroleum has never been fully determined (Smith et al. 1975). Available information indicates that about 90 percent of the metals content is retained in heavier residue fractions during fractionation (Smith et al. 1975). Much residual fuel oil is consumed in various industrial facilities and within the refinery itself, but the largest portion is consumed by electric power plants. After combustion, a substantial portion of the oil's metal content remains in the bottom ash or is emitted in fly ash. The more volatile metals, metal oxides, and finer particulates may be released into the atmosphere. Few data are available to account for the environmental transport and ultimate fate of these metals. Bottom ash may be used as an aggregate material for road construction, concrete, and other similar purposes. Collected fly ash has less commercial value, and, like unused bottom ash, may be discarded as solid waste. Metals in fly ash occur primarily as metal oxides, which are generally susceptible to solubilization and leaching and may contaminate ground and surface waters.

There are not enough reliable data concerning the disposition and behavior of petroleum-associated metal compounds to predict their environmental fate and effects. The fate and significance of metals entering the environment from refinery-associated operations, especially solid and liquid waste streams, require further study. Basic knowledge concerning metals toxicity, physiological roles, environmental transport, environmental effects, occupational health hazards, and pathways through the food chain is required to assess the relative hazards.

Metal Carbonyls

Metal carbonyls--substances in which carbonyl (CO-) radicals are covalently bonded to a metal atom--may pose significant hazards to exposed refinery workers and those in the immediate area. Metal carbonyls form by reaction of carbon monoxide with transition series metals under certain conditions of temperature and pressure. Hydrogen and nitrogen gases, which are used extensively in refinery operations, often contain trace amounts of carbon monoxide (CO). Nitrogen gas is frequently used as an inert gas in processes involving hydrogen, such as hydrotreating, to prevent reactive oxygen (air) from entering the reaction chambers. The nitrogen may contain up to 0.6 percent CO and the hydrogen gases may contain up to 3 percent CO (Brief et al. 1971). Under conditions of high temperature and pressure encountered in refinery operations, CO may react with nickel, cobalt, and iron from catalysts and piping. The resulting carbonyls are unstable in the air at ambient temperatures--nickel carbonyl $[\text{Ni}(\text{CO})_4]$ has an estimated half-life of about 11 minutes and cobalt carbonyl $[\text{Co}(\text{CO})_4]$ has a half-life of 10 to 15 seconds (Brief et al. 1971). In more recent work, parts per million concentrations of nickel carbonyl in the absence of CO have been found to have a lifetime of less than 1 minute (Stedman et al. 1980). The presence of CO increases the lifetime by about 1/2 minute for every part per million of additional CO. These volatile carbonyls have high vapor pressures.

Nickel carbonyl is the most readily formed and the most toxic metal carbonyl. It is acutely toxic by both dermal and inhalation routes. No clear estimate is available of the dose producing acute effects in man, but a 30-ppm-exposure in air for 30 minutes is reported to have been lethal. Chronic exposure to lower levels of nickel carbonyl has been shown to cause sinus and lung cancer in epidemiological studies and in laboratory experiments with several species. Chronic exposure may also lead to severe dermatitis.

Refinery workers may be exposed to carbonyls during the termination and initiation of operations, and during maintenance, since metal carbonyls may be present in process streams. The odor threshold for nickel carbonyl is 1 to 3 ppm--well above safe exposure levels. Reliable and quick methods to detect personal exposure to carbonyls in the workplace are not available, nor are data available concerning concentrations encountered by workers in refinery operations.

The Occupational Safety and Health Administration has established a TWA of seven micrograms per cubic meter for nickel carbonyl.

Platinosis

Platinum and other precious metal catalysts are used extensively in catalytic reforming and hydrotreating. Information concerning catalysts is largely proprietary, but most probably involve platinum, chloroplatinic acids, or other precious metal complexes fixed on alumina or silica. Catalysts must be periodically removed for regeneration or recycling, during which workers may be exposed to these compounds. Platinosis is a disease involving allergic respiratory and cutaneous reactions from contact with or inhalation of chloroplatinic acid and other platinum salts, but not metallic platinum (Parrot et al. 1969). Exposure of susceptible individuals results in recurrent, persistent asthma and eczema.

Most reported cases of platinosis are associated with platinum and precious metals refining. The incidence of this disease and other catalyst adverse reactions among refinery workers is unknown.

Dioxins

A recent Dow Chemical Corporation report asserts that chlorinated dioxins may be formed in trace amounts during the combustion of organic matter and fossil fuels, including refined petroleum products (Chlorinated Dioxin Task Force 1978). These chlorinated dibenzo-p-dioxins include many highly toxic isomers, such as the more extensively studied 2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD), one of the most toxic substances known to man. Chlorinated dioxins have been postulated to form during combustion from the condensation of chlorophenols and by thermal synthesis from inorganic chloride and hydrocarbons.

Petroleum refining juxtaposes many materials, factors, and processes that may contribute to the formation of chlorinated dioxins: steam; heat; a wide variety of hydrocarbons; phenolics; catalytic and thermal cracking; catalytic reformation; pressure; combustion for catalyst regeneration; and inorganic chloride from water, crude oil salt content, and HCl and chlorides used in various processes. There have been no reports of chlorinated dioxin and halogenated dibenzo furan concentrations associated with various refinery process and effluent streams.

Summary of Research Needs

The area of health effects research related to refineries is just beginning to receive substantial attention with respect to Federally-funded, energy-related research. This is primarily due to the fact that the development of a responsive Federal program of health research related to energy technologies has focused on

emerging energy technologies such as synthetic fuels and solar energy technologies. Research concerning conventional technologies (coal, oil, and gas) has focused on the fossil based extraction and end use facets of the industries. Perhaps another reason that refineries have not received significant attention in terms of energy-related health and environmental research is that refineries, like most industrial facilities, have been subjected to stringent air and water pollution control regulations for many years.

Federally-funded, energy-related research began during the 1978 fiscal year with the initiation of two projects, coordinated by the U.S. Department of Energy and the National Institute for Occupational Safety and Health. The Department of Energy project recognizes that there are poorly defined reports of elevated cancer mortality rates in many areas, including Contra Costa County, California, a major refining center. The study, accompanied by modest funding, is intended to focus on a number of disorders, concentrating at first on cancer, cardiovascular, and respiratory disorders among refinery workers. The second study involves the development of a program to identify and quantify worker exposures to potentially hazardous agents in refineries and to provide baseline data for the development of control measures. This effort also has received limited funding.

Integrated Health Assessment

As seen from the numerous pages in the preceding discussion of potential health effects associated with petroleum refining, there is a voluminous amount of relevant data available in the public domain. Still more data exists as proprietary information concerning catalysts, process chemicals, and in-plant, company-sponsored emissions and ambient monitoring studies. A great deal of information, generally in the basic effects research category, still needs to be amassed.

All of these data--whether missing, existent but not available, or published--present a fragmented and incomplete picture of the health and safety risks in the refinery industry as a whole. An intensive, major effort is needed to bring all of this information together in an attempt to conduct a rigorous risk assessment. Such an activity would be large in scope and diverse in its approach.

In addition to information collected from published articles on the toxicity and exposure levels of various refinery emissions, a data base should be developed containing the results of epidemiological studies already conducted that are relevant to refineries. Retrospective mortality studies of refinery workers should be initiated. The resultant data and registry of workers would provide the basis for risk assessment studies.

This comprehensive assessment of risks associated with the refinery industry should include individuals working and living around refinery sites. It is important in such a study to use and associate data on emissions of pollutants from a refinery with various vectors of transport to estimate population exposure and possible resultant health impacts.

Emissions estimates for pollutants from refinery operations and their uptake and transport by water, food, wind, and rain should be compiled to facilitate an adequate estimate of exposure and health impacts of refinery operations on nearby communities and ecosystems. This work should be site-specific, perhaps using a grid system to model emission measurements and resultant exposures. The quality and availability of epidemiological data through state registers should be considered in selecting sites for assessment studies. The monitoring data should be correlated with the epidemiological data of persons living and working in the modeled region. Abnormal increases in illnesses, miscarriages, birth defects, or deaths should be noted and investigated.

The comprehensive health assessment activity needs to receive input and coordination from the many organizational entities having jurisdiction over or an interest in the health of persons who work or live in or near refinery complexes. These entities include, but are not limited to, the Department of Energy; the Environmental Protection Agency; the National Institute for Occupational Safety and Health; the Occupational Safety and Health Administration; the National Petroleum Refiners Association; the American Petroleum Institute; the Oil, Chemical and Atomic Workers International Union (AFL-CIO); and refining companies.

Specific Basic Research Needs

The textual discussion has identified numerous gaps in our understanding of the health effects of various hydrocarbon species. Much of the information that is available is of a generic nature, i.e., it is also useful to the understanding of the effects of hydrocarbons emanating from other technologies such as synthetic fuels and chemical coal cleaning. The reader should review the textual discussion in depth to decide whether extensive additional research in these areas is needed to resolve the particular health problems associated with refineries. A partial listing of basic information needs follows:

- o The extent of biologically-based monitoring in the refining industry is unknown. Biologically-based monitoring of individual worker exposures through measurement of substances

or their metabolites in body fluids, excretions, and hair are available only for a limited number of toxic substances. A survey is needed to identify the extent of current monitoring, to amass a data base of monitoring findings, and to recommend expanded monitoring programs. The initial focus should be on the presence of representative mixtures.

- o The cause of the hemodynamic effects of propane, butane, and isobutane is unknown. These chemicals may act directly on the vascular system or via the central nervous system depression. This problem area needs to be explored.
- o The complex mixtures of substances encountered in the refinery require toxicological testing.
- o It is unknown whether toluene modifies the neurotoxic actions of hexane or whether short-term, high concentrations of hexane-toluene mixtures are responsible for neuropathy. Information in this area would be useful, not only for understanding health effects problems related to refinery workers, but also for mitigating the degradation of the health of glue-sniffers.
- o As exposure to pure hydrocarbons is rare, studies are needed which investigate synergistic and other interactive neurotoxic effects among constituents of mixtures of hydrocarbons and other agents (e.g., gases, metals) commonly present in the workplace environment.
- o Hydrocarbon-induced neuropathies require further study to determine underlying causes and mechanisms of neurotoxicity.
- o Epidemiological studies designed to characterize exposures to toluene and xylene do not exist. These would be important and should be conducted to provide input to risk assessment studies.
- o Data on the reproductive and teratogenic effects of thiols are not available. Several studies suggest a potential human mutagenic effect, but these studies involved simultaneous exposure to chloroprene, a known mutagen. Carcinogenic effects have not been investigated. No epidemiological studies concerning thiols are available, nor are data concerning exposures to thiols within petroleum refineries. These data gaps should be filled.
- o Nitrilotriacetic acid (NTA) is a chelating agent used as a scale preventative in cooling water. This is a potential

nitrosating chemical and the level of its use in refineries for scale prevention and chelation during crude desalting or wastewater treatment should be determined.

- o Metals and metal oxides present major fugitive emissions, solid waste, and effluent problems for refineries, yet few data are available to account for the environmental transport and fate of these metals from a health hazard point of view. This area needs to be explored.
- o Reliable and quick methods to detect personal exposure to toxic metal carbonyls in the workplace are not generally available, nor are data concerning carbonyl concentrations encountered by workers in refinery operations. This area needs substantial research.
- o Platinosis is a disease involving allergic respiratory and cutaneous reactions from contact with or inhalation of chloroplatinic acid and other platinum salts. Most reported cases of platinosis are associated with platinum and precious metal refining. The incidence of this disease and other adverse reactions to platinum and other catalysts among refinery workers should be investigated.
- o Petroleum refining utilizes many materials under conditions that may contribute to the formation of toxic chlorinated dioxins. The presence of and concentrations of chlorinated dioxins and halogenated dibenzofurans should be determined with respect to the refinery workplace environment, process streams, and wastewater effluents.
- o Workers' exposures to refinery process and waste streams and chemicals should be examined to devise appropriate and accurate means of assessing exposures to toxic agents.

Occupational Health

Brain Cancer and Refinery Workers. Reports have recently appeared in the popular press concerning large numbers of brain tumor deaths occurring among workers at several Gulf Coast petroleum refineries and petrochemical complexes. So far, at one facility 18 brain cancer deaths between 1956 and 1980 have been identified among male workers. This is roughly twice the number expected among workers at the plant and investigators believe this to be the largest single series of presumably occupationally-related brain tumors to date (Chemical and Engineering News 1980a). Another study reported a similar high incidence and risk of brain cancer (approximately double the normal) at several other sites, including three refineries. These studies are still in progress or have not been published.

Available epidemiological studies appear to indicate a high proportionate mortality ratio or high incidence of brain tumor deaths among workers at a number of Gulf Coast refineries and petrochemical complexes, but the significance of these findings is not clear. Several case control studies comparing tumor victims to employees with similar job histories have found no significant increased risk. No specific areas, processes, work classes, or agents have been implicated to date. One conflicting study has found no significant increased incidence of brain tumors at one of the refineries reported to have a high incidence. This retrospective cohort study was conducted at a Texas refinery with 44 years of employment experience and it claims to be the largest study of its kind in North America in terms of years of operation and person-years observed. Similarly, other preliminary studies and analyses, most performed by affected industrial concerns, refute findings of high incidence and risk of brain tumor mortality.

A recent mortality study of workers at eight refineries in the United Kingdom found no significant increased risk for brain cancer, but above normal incidences of malignant melanoma (skin cancer) and esophageal, stomach, intestinal, and rectal cancers (Rushton and Alderson 1980).

The relative increased risk and the linkage of brain tumors with employment in the petroleum refining and petrochemical industries requires further examination. However, it may not be possible to resolve the issue, and it may not be relevant to these industries under current industrial hygiene practices (Chemical and Engineering News 1980b). Most observed mortality cases involve workers who began employment more than 30 years ago, prior to significant changes in petroleum refining and work practices. Variations in methodology, data validity and availability, and investigators' professional commitments will result in the questioning of results and conclusions from these and most epidemiological studies. An increased understanding of brain tumor initiation and reliable animal models and testing systems relevant to human risk assessment should be developed. Coordinated research, especially epidemiological study, is required to determine the extent and cause of petrochemical-related occupational concerns. It is possible that a new workplace hazard, akin to the now-recognized threat posed by vinyl chloride exposure, may be recognized and defined.

Data Reporting for Non-refinery Employees. Many workers such as contractor employees, construction workers, part-time employees, railroad workers, and truck drivers may work within the boundary of a refinery site and may be exposed to its hazards. Normally, data concerning industrial refinery accidents, diseases, chemical rashes, neurological disorders, and incidences of exposure do not extend to these workers, even when they may work on site on a full time basis.

A reporting mechanism should be initiated for the refining industry that will include these individuals. The collected data should be aggregated with similar data for refinery employees. This information would serve as a data base for future health assessment activities.

Industrial Hygiene. There is a need to develop criteria for refinery workers' medical examinations that will identify persons with special sensitivities to stresses present in refinery facilities. The criteria should be implemented industry-wide and they should focus on physiological and psychological changes that are precursors of occupational diseases. Since human behavior can be affected by exposure to a wide variety of metals, organic solvents, and noxious gases, the identification of behavioral and neurotoxic effects should be a high priority.

Detection of Dermal Exposure. The current method for detecting the presence of polynuclear aromatic hydrocarbons (possible carcinogens) on the skin of workers involves detection with ultraviolet light. This method may introduce the potential for photoactivation (see text discussion) of the compounds present on the skin surface. Although the resultant health risk is far lower than that from exposure to sunlight for a few minutes, an additional margin of safety could be introduced if alternative detection methods were available.

Of utmost importance is the development of a safe and effective decontamination procedure for removing organic compounds from the skin and clothing on a daily basis. The development of such a procedure is important, not only to worker health, but also to ensure that the contamination is not carried home to workers' families.

Public Health--Community Surveillance

The surveillance and monitoring of communities that may be impacted adversely by refinery operations should be maintained and expanded. The incidences of disease in these communities should be monitored and significant differences should prompt in-depth investigations.

Existing registries of the prevalence of cancer, heart disease, birth defects, and neurological disorders should be examined to determine whether disease trends can be detected for communities near refineries. If not available, such minimal statistics as births, deaths, year, cause, and age should be amassed to provide a data base

for continuing assessment. In this light, a review of the adequacy of existing registries should be conducted. The registries should be expanded, if necessary, to assure the adequacy of data-base coverage and comparability with occupational and other related registries.

ECOLOGICAL EFFECTS OF REFINERY OPERATIONS

Aquatic Biota

Refined oils may be much more toxic than crude oils when released into marine or surface waters. Crude oils are rapidly altered by weathering phenomena involving evaporation, dissolution, microbial decomposition, and chemical oxidation. Low-boiling, highly toxic fractions in crude oils are rapidly depleted, frequently in 2 to 4 days. Refined petroleum products such as gasoline and fuel oils contain greater percentages of these toxic, low-boiling fractions. The toxic effects of spilled crude and refined petroleum products are discussed at length in the Transportation and Storage section of this report.

Long-term, continuous-flow bioassays of biologically treated oil refinery effluents indicate that refineries produce effluents which contain substances causing cumulative toxic effects in fish (National Academy of Sciences 1972). Passage of treated effluents through activated carbon columns does not significantly remove the fish toxicants. Compounds implicated are C₁₁ through C₁₈ alkanes and phenolic compounds, and isomers of cresol and xyleneol.

Sedimented oil has been found downstream from refineries. Sediment in the Ottawa River in Ohio downstream from a refinery consisted of up to 17.8 percent oil (National Academy of Sciences 1972). Sedimented oil may slowly release its hydrocarbon, metallic, and other constituents to the aquatic environment and may act as a concentrator for hydrocarbon-soluble substances such as chlorinated hydrocarbon pesticides. Metal compounds from refinery effluents may become sedimented. They also may remain suspended in water in particulate form. Sedimented metals and hydrocarbons can be redissolved or resuspended, especially if sediment is physically disturbed.

Soluble aromatic hydrocarbons, which may enter surface waters through wastewater discharges, runoff, or deposition of atmospheric emissions from refineries, can affect many forms of aquatic biota. Table 20 provides comparisons of the toxic levels of these hydrocarbons as they affect various biota.

Phenolics may be major pollutants in surface and drinking water. They adversely affect the organoleptic (odor and taste) characteristics of drinking water, usually at concentrations of less than 1 ppm (1 mg per liter), and may taint the flesh of fish. Cresol has a threshold concentration of 0.055 mg per liter in water (National Academy of Sciences 1972). Phenolic-bearing water, when chlorinated for drinking water disinfection or wastewater treatment, yields chlorinated phenols that have much lower odor/taste threshold

TABLE 20

TOXICITY OF SOLUBLE AROMATIC HYDROCARBONS

Group of Organisms	Estimated Concentration (ppm) of Soluble Aromatics Causing Toxicity ^a	Estimated Amount (ppm) of Petroleum Substances Containing Equivalent Amount of Aromatics	
		Number 2 Fuel Oil	Fresh Crude
Flora	10 - 100	50 - 500	$10^4 - 10^5$
Finfish	5 - 50	25 - 250	$10^4 - 10^5$
Larvae (all species)	0.1 - 1.0	0.5 - 5	$10^2 - 10^3$
Pelagic crustaceans	1 - 10	5 - 50	$10^3 - 10^4$
Gastropods (snails)	10 - 100	50 - 500	$10^4 - 10^5$
Bivalves (oysters, clams)	5 - 50	25 - 250	$10^4 - 10^5$
Benthic crustaceans (lobsters, crabs)	1 - 10	5 - 50	$10^3 - 10^4$
Other benthic invertebrates (worms)	1 - 10	5 - 50	$10^3 - 10^4$

^a Not inclusive of all members of each group due to limited data base.

Source: Britt and Hushon 1976.

concentrations: 2-chlorophenol (2 ug per liter), and 4-chlorophenol (250 ug per liter). Because treatment processes such as chlorination may increase the odor and toxicity of phenolic compounds, it is recommended that public water supply sources contain no more than 1 ug per liter of these compounds (National Academy of Sciences 1972).

Effluents from the refinery may include complex phenolic mixtures whose adverse aquatic effects may vary over a wide range, depending on the substances, concentrations of their components, and environmental conditions. Many phenolics, especially chlorinated derivatives, are more toxic than phenol itself. Phenol toxicity varies greatly with fish species (0.079 mg per liter in 30 minutes for minnows, and 56 mg per liter in 96 hours in mosquito fish, or Gambusia affinis) (National Academy of Sciences 1972). The phenolic and other compounds that taint or adversely affect the taste of fish at low concentrations are shown in Table 21.

Terrestrial Biota

Solid Wastes

Refineries typically produce a number of process-related solid wastes, including (Rosenberg 1976):

- (1) Crude oil tank bottoms,
- (2) Leaded gasoline tank bottoms,
- (3) API and other oil-water separator sludge,
- (4) Neutralized hydrofluoric acid alkylation sludge,
- (5) Kerosene filter clays,
- (6) Cooling water sludge,
- (7) Dissolved air floatation skimmings,
- (8) Spent lime from boiler feedwater treatment (acid neutralization),
- (9) Spent amine solids,
- (10) Exchanger cleaning sludge,
- (11) Waste biological processing sludge,
- (12) Silt from stormwater runoff,

TABLE 21

REFINERY EFFLUENT COMPONENTS THAT CAN CAUSE
TAINTING OF THE FLESH OF AQUATIC ORGANISMS

Chemical	Estimated Threshold Level in Water ^a (mg/l)
Acetophenone	0.5
Cresol	0.07
M-cresol	0.2
O-cresol	0.4
P-cresol	0.12
Cresylic acid (meta para)	0.2
N-butylmercaptan	0.06
O-sec. butylphenol	0.3
P-tert. butylphenol	0.03
O-chlorophenol	0.0001 to 0.015
P-chlorophenol	0.01 to 0.05
2,3-Dichlorophenol	0.084
2,4-Dichlorophenol	0.001 to 0.014
2,5-Dichlorophenol	0.023
2,6-Dichlorophenol	0.035
2-Methyl, 4-chlorophenol	0.075
2-Methyl, 6-chlorophenol	0.003
O-phenylphenol	1
2, 4; 6-Trichlorophenol	0.003 to 0.05
Phenol	1 to 10
Phenols in polluted water	0.02 to 0.15
Diphenyl oxide	0.05
O-dichlorobenzene	0.25
Ethylbenzene	<0.25
Ethanethiol	0.24
Formaldehyde	95
Kerosene	0.1
Kerosene plus kaolin	1
Isopropylbenzene	<0.25
Naphtha	0.1
Naphthalene	1
Naphthol	0.5
2-Naphthol	0.3
Dimethylamine	7
Oil, emulsifiable	<15
Pyridene	5 to 28
Pyrocatechol	0.8 to 5
Quinoline	0.5 to 1
P-quinone	0.5
Styrene	0.25
Toluene	0.25

^aThe threshold is the concentration in water at which the effluent component can cause tainting of the flesh of fish and other aquatic organisms.

Source: National Academy of Sciences 1972.

- (13) Fluid catalytic cracker catalyst fines,
- (14) Coke fines,
- (15) Lube oil filter clays,
- (16) Spent catalysts,
- (17) Chemical precipitation sludges,
- (18) Vacuum or centrifuge filtration sludge, and
- (19) Silica gel and other filtration media.

Recent estimates of the amounts of each solid waste stream are shown in Table 22. Note the degree of uncertainty associated with these values.

The first 13 wastes listed above are typically produced by topping and all other types of refineries. Cracking, petrochemical, and integrated refineries also generate fluid catalytic cracking (FCC) fines and coke fines. Lube refineries generate lubricating oil filter clay wastes. Spent metallic catalysts may not be refinery wastes, for many undergo off-site reprocessing to recover their precious metals content. Chemical precipitation sludges, silica gel, and other filtration media will usually be waste products from refineries with tertiary wastewater treatment systems.

A number of variables affect the compositions and quantities of wastes produced by a refinery. One of the major variables is the crude oil feedstock. Crude oil heavy metals content will significantly affect the metals content of crude oil storage tank bottoms and a number of other wastes. Another set of variables involves the mix of processes performed at the refinery. For example, hydrofluoric acid and sulfuric acid alkylation units generate distinctly different wastes. As noted above, the processes used at refineries vary greatly. This contributes to a wide variation in the quantity and constituents of wastes among refineries.

Air and water pollution control processes are a major solid waste determinant (Rosenberg et al. 1976). For example, the use of electrostatic precipitation units in conjunction with fluid catalytic cracking catalyst regeneration removes particulate matter that would otherwise be an air emission. Hydrotreating, rather than using clay filters to remove sulfur, decreases the amount of solid waste produced. Operational practices and the condition of individual process units may significantly affect the amounts of wastes produced.

TABLE 22

ANNUAL SOLID WASTE GENERATION
OF THE U.S. PETROLEUM REFINING INDUSTRY

Stream	Total Generation (metric tons/year)	95% Confidence Interval for Total Generation (metric tons/year)	
Slop oil emulsion solids	59,380	9,690 -	28,720
Silt from storm water runoff	139,900	16,390 -	923,200
Exchanger bundle cleaning sludge	690	90 -	3,700
API separator sludge	51,090	21,500 -	94,090
Nonleaded gasoline tank bottoms	900	80 -	72,200
Crude tank bottoms	14,450	2,470 -	56,460
Other storage tank bottoms	21,500	230 -	149,800
Leaded gasoline tank bottoms	4,400	1,070 -	13,920
Dissolved air flotation skimmings	76,110	24,670 -	174,400
Kerosene filter clays	2,470	550 -	8,100
Other filter clays	44,930	4,230 -	378,800
HF alkylation sludge	34,180	2,100 -	421,100
Waste bio-sludge	97,790	22,380 -	361,200
Once-through cooling water sludge	2,470	0 -	47,570
FCC catalyst	99,370	37,000 -	123,300
Coke fines	35,770	880 -	815,800
Spent amines	18	0 -	350
Salts from Regeneration	----	----	----
Ship and barge ballast	----	----	----
Other	2,290	140 -	23,300
Total	687,708	143,470 -	3,695,950

Note: ----Represents data not available

Source: Galloway 1979.

Industry-wide, annual estimates of constituents of refinery solid wastes have been developed (Rosenberg et al. 1976). Tables 23 and 24 present 1974 and 1983 estimates of constituents of all refinery solid wastes. Individual waste streams contain higher concentrations of particular waste constituents. Oil is the principal component of refinery wastes, representing approximately 110,000 metric tons per year. About 250 metric tons of metallic compounds are annually contained in refinery wastes: 87 metric tons (35 percent) chromium; 78 metric tons (31 percent) zinc; 23 metric tons (9 percent) nickel; 22 metric tons (9 percent) copper; and 20 metric tons (8 percent) vanadium. The remaining 9 percent consists primarily of lead, arsenic, molybdenum, cobalt, selenium, mercury, silver, and cadmium. Additional waste estimates are 812 metric tons of fluorides, 5 metric tons of phenols, 1 metric ton of cyanide, and 0.1 metric ton of benzo(a)pyrene. Recovery of strategic metals such as chromium from refinery wastes is apparently not yet an economical proposition for it is not a common practice.

Solid Waste Disposal. An estimated 687,708 metric tons per year of solid waste (dry weight) is generated by U.S. petroleum refineries (Galloway 1979). Current final disposal technologies include on-site or off-site landfilling, landfarming, and to a lesser extent, incineration, deep well and salt mine disposal, ocean dumping, and lagooning. Results of a survey of waste disposal methods at 19 refineries in 1973 and projections for 1983 are shown in Table 25. Treatments currently used (prior to ultimate disposal) include: vacuum filtration, pressure filtration, centrifugation, dewatering lagoons, aerobic digestion, anaerobic digestion, and chemical fixation. Predisposal solid waste treatments are primarily used to dewater (concentrate) solid wastes, and perform some biodegradation.

As shown in Table 25, in 1973, 44.3 percent of all solid wastes were disposed of on site, versus 55.7 percent disposed of off site. Projections for 1983 indicate a significant increase in the amount of solid waste disposed of on site versus off site, a decrease in lagooning, and a major increase in the amount of on-site landspreading (landfarming). Increased on-site landspreading is the major factor responsible for the decrease in off-site disposal, from 55.7 percent in 1973 to 27 percent in 1983. Little is known about current refinery waste disposal practices.

A number of factors are influencing the trend toward on-site disposal:

- o The closing of many off-site dumps, lagoons, landfills, and other disposal sites;
- o Increasingly stringent regulatory actions, public scrutiny, and adverse opinion concerning waste disposal practices;

TABLE 23

WASTE CONSTITUENTS GENERATED BY REFINERIES
(1974)

Waste Constituents	Total Waste (dry weight metric tons/year)
Phenol	5.3367
Cyanide	1.07532
Selenium	1.50562
Arsenic	2.07518
Mercury	0.44461
Beryllium	0.076327
Vanadium	19.8619
Chromium	87.782
Cobalt	2.70868
Nickel	23.4657
Copper	22.0568
Zinc	78.177
Silver	0.52749
Cadmium	0.193626
Lead	14.5644
Molybdenum	2.13429
Ammonia	4.9334
Polynuclear aromatic hydrocarbons	0.112573
Oil	109,806
Sulfur	811.90

Source: Rosenberg et al. 1978.

TABLE 24

ESTIMATES OF REFINERY WASTE GENERATION
(1983)

Waste Constituent	Total Waste (dry weight metric tons/day)
Phenol	7.28
Cyanide	1.40684
Selenium	2.0912
Arsenic	2.48803
Mercury	0.58041
Beryllium	0.102325
Vanadium	30.7632
Chromium	75.144
Cobalt	2.87359
Nickel	33.736
Copper	21.7729
Zinc	69.980
Silver	0.69295
Cadmium	0.203681
Lead	16.4492
Molybdenum	2.27229
Ammonia	4.1432
Polynuclear aromatic hydrocarbons	0.152803
Oil	112,238
Sulfur	1,044.99

Source: Rosenberg et al. 1978.

TABLE 25

ESTIMATES OF REFINERY WASTE DISPOSAL METHODOLOGIES

Disposal Procedure	1973		1983	
	Onsite (%)	Offsite (%)	Onsite (%)	Offsite (%)
Landfilling	16.8	34.3	24	20
Lagooning	18.3	21.4	12	7
Incineration	0.8	0	3	0
Landspreading	8.4	0	34	0
Total	44.3	55.7	73	27

Source: Rosenberg et al. 1976.

- o Increased transportation costs and distances to certified dumping sites;
- o Increasingly stringent air and water emission regulations, which make less-regulated land disposal more attractive; and
- o A trend toward corporate and plant self-sufficiency, especially in waste disposal practices.

Some of the trends tending to increase the amount and change the constituents of refinery solid wastes include

- o Increased crude oil processing capacity;
- o Increased use of fluid catalytic cracking, hydrotreating, alkylation, and other solid waste producing processes;
- o Changes in crude oil feeds, especially an increased use of heavy and sour (high sulfur) crudes;
- o Increased use of biological treatment, air flotation, and tertiary wastewater treatment systems in response to government regulations; and
- o Increased enhanced oil recovery methods for crude oil extraction.

Some of the minor trends tending to decrease the amount and change the constituents of refinery solid wastes include:

- o A reduction in separated oil emulsion solid wastes due to increased refinery oil recovery and recycling;
- o Regulations reducing the use of lead compounds in gasoline; and
- o Reduced levels of chromium and zinc concentrations as corrosion inhibitors in cooling tower water due to environmental concerns.

While treated wastewater effluents from modern refineries tend to be relatively uniform and chemical analysis program results are available, the nature and quantity of solid wastes are highly variable and not well documented. Many refinery solid wastes are only intermittently generated--their volume and accumulation periods largely governed by process unit designs and individual refinery housekeeping and waste management practices. Continuously generated

wastes (those requiring disposal at less than 2-week intervals) generally result from major refinery processes and include (Sittig 1978):

- o Coking unit wastes--coke fines, spilled coke from unloading operations;
- o Spent catalyst and catalyst fines from fluid catalytic cracking catalyst regenerators;
- o Spent and spilled grease and wax wastes, especially in lube oil processing units;
- o Dissolved air flotation float;
- o Waste biological sludges; and
- o Slop oil (considered as a solid waste due to treatment and disposal practices).

Wastewater treatment yields a high volume and variety of solids and emulsions requiring disposal. These wastes are generated largely as a function of refinery throughput and wastewater processing. Oily solids and slop oils usually undergo emulsion breaking and filtration or centrifugation steps to remove water and recoverable oil. Sludges may be dewatered to facilitate transport.

Most off-site disposal is handled by private contractors. Recent changes in record-keeping and other requirements issued under the Resource Conservation and Recovery Act (RCRA) for handling hazardous solid wastes should make more information available concerning refinery solid waste disposal practices.

Environmental Effects of Solid Waste Disposal. The environmental adequacy of the treatment and disposal methods employed by the petroleum refining industry varies greatly, much the same as it does with the rest of the nation's industries (Rosenberg et al. 1976). Major environmental hazards from refinery solid waste disposal are ground and surface water contamination and volatile emissions. Mandatory minimum requirements for off-site management are generally monitored by state or local regulatory agencies. Disposal sites typically operate under renewable permits. Off-site landfilling operations are increasingly being required to monitor groundwater quality. Some on-site landfills use bentonite clays or other linings with presumed high ion exchange capabilities and low permeability under their landfill sites, but some do not.

Landfarming or landspreading involves the spreading and mixing of the wastes into surface soil for biodegradation of organic material by soil bacteria. Land requirements for landspreading depend on the soil's oil-loading potential and the amount of oil in the wastes. In many cases, landfarming may improve soil texture and fertility, however the suitability of growing food crops on land-farmed soils requires scrutiny. Field test plots have shown that climate has little long-term effect on oil degradation--the cold and arid climate of Montana and the warm and humid climate of the Gulf Coast states support landfarming (Kincannon 1976; Huddleston and Cresswell 1976). Safeguards observed in 1974 were limited to the construction of rainwater runoff-preventing dikes and low-level berms surrounding spreading areas (Rosenberg et al. 1976). During that year, only one surveyed facility utilized monitoring wells, a program for leachate detection, and an analysis program to identify intermediate degradation by-products.

Landfill and landspreading monitoring programs may not prevent contamination of local groundwaters. Monitoring networks must be carefully designed. Chemical identities and solubilities may change with time in the complex chemical and bacterial environment of soils. Little information is available concerning the transformations refinery wastes undergo in various soils. It is nearly impossible to remove contamination once it has reached an aquifer.

The majority of lagoons observed in 1974 were constructed from native earth materials and the only safeguards observed were the occasional use of concrete, plastic, and clay liners to reduce or impede exfiltration of hazardous liquids.

Incineration is one method for disposing of organic solid wastes. It has advantages of being free from most objectionable odors and independent of weather conditions, and it facilitates a high reduction in the volume of solid wastes requiring disposal. However, incinerators require considerable capital and operating expenditures, and may require supplemental fuel if the solids have a heat content of less than 10,000 Btu's per pound. Multiple hearth and fluidized-bed incinerators are the most commonly used. Air pollution scrubbing systems are frequently required and ash must still be disposed of as solid waste.

Refineries with a high level of water intake and wastewater effluent treatment may generate solid wastes high in inorganic salts. High salt-containing wastes result from:

- o Treatment of brine (mostly sodium chloride) from crude desalting operations;

- o Rinsing and regeneration of ion exchange resins used to pretreat water for steam generation; and
- o Cooling tower and boiler blowdown concentrates (salts in raw water supply plus any additives used).

Resulting inorganic salts, mostly sodium, calcium, magnesium, and other salts present in the raw water supply, are not amenable to disposal by most landfill or landfarming methods. Most of these salts are deliquescent, absorbing atmospheric moisture and ultimately dissolving and leaching into groundwater or running off into nearby bodies of water. Potential impacts include the killing of terrestrial vegetation, impairment of water quality for public and industrial uses, and adverse effects on aquatic ecosystems. These wastes may not be disposed of in impervious clay containment basins, as they tend to destroy the clay's impervious characteristics. Inorganic salts are not amenable to disposal by incineration. The only acceptable methods for disposing of these inorganic salts are by ocean dumping (if they do not contain high concentrations of other toxic wastes), disposal in plastic-lined or sealed basins, and disposal in salt mines.

Certain precautions are exercised in the disposal of leaded gasoline sludges and residues. Special breathing and ventilation systems are required to protect workers within tanks and when handling these materials. The sludge reportedly is placed on elevated outdoor concrete slabs with a peripheral curbing. The entire slab is sloped and it drains to the refinery wastewater collection system. Presumably, lead and other compounds in the sludge are permitted to partially wash into the wastewater treatment system while they are dried prior to final disposal, probably in landfills.

Only landfarming can truly be considered an ultimate land-based disposal technique because the wastes are degraded and become incorporated into the soil (Galloway 1979). Although anaerobic degradation theoretically occurs in landfills, some recently reopened landfills show no significant anaerobic digestion of oily wastes. Lagooning, disposal wells, salt mine disposal, and ocean dumping do not foster biodegradation. All of these, except ocean dumping, are long-term storage techniques. Incineration is energy and capital intensive, and generates air pollutants and ash residues requiring solid waste disposal. Optimum methods for disposing of refinery solid wastes require further study and discussion.

The total hydrocarbon content of refinery solid wastes has recently been estimated at 190,000 tons per year (dry weight) (Galloway 1979). Four waste streams contain about 75 percent of these

hydrocarbons: dissolved air flotation skimmings, slop oil emulsion solids, API separator sludge, and waste biological processing sludge. Data concerning hydrocarbon volatility and volatile organic compound emissions from disposed solid wastes are not available.

Safeguards, such as encapsulation in plastic or concrete, burial in steel drums, and leachate analysis and treatment, were not observed in 1974 according to the study of refinery wastes disposal. "The industry simply believes that this type of treatment and/or handling is not warranted or economically justified" (Rosenberg et al. 1976). The recent implementation of the Resource Conservation and Recovery Act (RCRA) and increased corporate and public awareness of the hazards associated with solid waste disposal will probably result in the availability of more information on this subject, fostering the development of better disposal practices and treatment facilities.

Effect of Air Emissions on Biota. Of the primary acyclic and alicyclic hydrocarbons, only ethylene has been found to significantly affect vegetation. The hydrocarbons most nearly approaching the activity of ethylene are acetylene and propylene. These gases require levels 60 to 500 times that of ethylene to produce similar adverse effects. At concentrations of 1 ppm or less, ethylene may be the only hydrocarbon harmful to vegetation (Britt and Hushon 1976).

Besides its phytotoxic effects, ethylene is also produced naturally by plants and functions as a hormone in regulating growth, development, and other processes such as the ripening of fruit.

Symptoms of ethylene toxicity include: growth reduction, decreased optical dominance, bud abscission (leaf fall), and flower deformities. Leaf damage includes growth abnormalities, yellowing, death of tissue (necrosis), and premature abscission (Britt and Hushon 1976).

Some mononuclear aromatic hydrocarbons inhibit or reduce photosynthesis in plants. The effects of benzene on different species of trees have led Russia to establish a permissible air pollution concentration of 0.031 ppm (0.1 mg per m³). An increase in the number of methyl groups on the benzene ring has been reported to enhance the phytotoxicity significantly. Therefore, benzene is less toxic than toluene, which in turn may be less toxic than other substituted alkyl benzenes (Walker 1976).

No substantial information has been reported to indicate that airborne polycyclic hydrocarbons affect vegetation, except by contaminating soil. However, they can be incorporated into vegetation by absorption from the soil through roots and may settle on exposed

surfaces. Although relatively non-toxic to plants at low concentrations, aromatic hydrocarbons may be air-oxidized to quinones which may be phytotoxic at a few parts per billion.

With regard to phenols, cresols are used as agents for breaking dormancy and as herbicides to destroy various plant tumors. The effects of airborne refinery emissions of phenols on plants is unknown.

The reader is referred to the Transportation and Storage section of this report for information concerning the effects of spilled crude oil and its refined products on terrestrial vegetation.

Summary of Research Needs

Aquatic Effects. The discharge of refinery liquid effluents into surface waters from point sources is regulated through the National Pollutant Discharge Elimination System (NPDES). Some of these discharges enter municipal sewage treatment systems. Uncontrolled runoff, leaching from disposal and storage areas, and atmospheric deposition deserve research as routes by which significant amounts of refinery hydrocarbons enter the aquatic environment.

The biological effects of aromatic hydrocarbons and phenols are well understood. Research emphasis should focus on the areas of their control and transport, transformation, and fate.

Terrestrial Effects. As one can see from the discussion above, airborne ethylene and phenols can have a detrimental effect on plant growth. Research is needed on the significance of this problem to fruit and vegetable growers. Fruit, vegetable, and other types of farms are located near many refinery sites. Research emphasis should be placed on the effects of these hydrocarbons on the retardation of plant growth, premature abscission, and dormancy breaking, as well as the impacts on farm animals and animal products.

Solid Wastes. The refining industry has made significant strides in recent years in the area of utilizing refinery wastes by landfarming. These innovations focus on using the soil environment for planned, orderly waste treatment. Research should be intensified in this area, with emphasis placed on: the precise nitrogen and phosphate requirements needed to landfarm oily wastes (this has economic implications); the types of vegetation that can be grown on oily waste land farms; the effects that factors such as plant growth have on the rate and extent of oil degradation; the demonstration that no hazardous substances are present or produced when oily wastes are landfarmed; and the degree to which toxic materials may enter plants and thus may pass through several food chains, affecting wildlife and possibly man.

TRANSPORT AND TRANSFORMATION

Air Medium

Air emissions vary greatly among refineries. Factors such as crude feedstocks, processes, equipment, air pollution control measures, housekeeping and maintenance practices, and the age and type of refinery strongly influence the amount and kinds of refinery-released air pollutants. Major air pollution sources within the refinery are:

- o Combustion sources--process heaters and boilers;
- o Process units--mainly fluid catalytic cracking catalyst regenerators, coking units, and asphalt blowing;
- o Storage and transfer activities; and
- o Wastewater and air pollution control and treatment systems.

Most available information and data regarding air pollutants concern regulated refinery pollutants, primarily sulfur oxides, particulate matter, nitrogen dioxide, carbon monoxide, and volatile organic compounds (hydrocarbons). In addition, aldehydes and ammonia have received attention. Table 26 presents air emissions estimates for several model refineries.

Unlike wastewater and liquid effluents, which are collected and usually combined for treatment, air emissions occur from a multitude of specific sources and are usually handled separately. Air pollution control systems, when used, are associated with specific process units and are usually designed to remove or modify specific pollutants. Wastewater effluent treatment processes tend to remove or reduce concentrations of many different types of compounds at once. The chemical content and disposition of refinery air emissions are less well-documented due to the multiplicity of sources within the refinery, the three-dimensional atmospheric dispersion of these pollutants, and regulations requiring comprehensive monitoring of select pollutants.

Environmental Transport

Air pollutants from petroleum refineries disperse in much the same way as other industrial airborne emissions. Concentrations of pollutants in the plant's immediate vicinity depend on the spatial distribution and physical characteristics of the emission sources. Combustion source stack emission height and emission temperature affect local ground concentrations of emissions--higher stacks and

TABLE 26

REFINERY AIR EMISSIONS

Pollutant	200,000 BPCD Fuel Oil Refinery Model ^a	200,000 BPCD Gasoline Refinery Model ^a	200,000 BPCD Gasoline Refinery (Reference) ^a
Particulates, lbs/hr	263	432 ^b	353
Sulfur dioxide (SO ₂), lbs/hr	667	948	1,918 ^c
Hydrocarbons (HC), lbs/hr	3,082	3,200	6,418 ^d
Carbon monoxide (CO), lbs/hr	50	95	138 ^e
Nitrogen oxides (NO _x), lbs/hr	493	1,250	1,846 ^e

^aBbl per calendar day average daily production.

^bExcessive particulate emissions are due to the combustion of some fuel oil in the gasoline refinery module, whereas only fuel gas is combusted in the reference refinery.

^cThe larger SO₂ emission rate is due to a larger volume of tail gas being emitted from the reference refinery, which is a result of a higher percentage of sulfur in the crude.

^dThe larger hydrocarbon rate is due to the greater crude and petroleum storage capacity in the reference refinery.

^eThese values are comparable on a size of refinery basis.

Source: Sittig 1978.

hotter emissions generally lead to lower ground concentrations. The trend toward maximum heat recovery may be lowering the temperatures of stack emissions and exacerbating combustion-related ground levels of pollutants. Fugitive emissions generally occur near ground level and, thus, may pose hazards to employees and those in the immediate area.

Meteorological factors are the primary determinants influencing dispersion of air pollutants. Concentrations of air pollutants are functions of dilution and diffusion processes. These depend largely on interrelated meteorological factors, such as atmospheric stability, wind speed and direction, mixing depth, temperature, humidity, precipitation, and inversions. Other local conditions such as terrain barriers may affect dispersion, possibly causing a buildup of pollutants in the vicinity of or downwind from the refinery. Insufficient information is available to make conclusions regarding a generalized distribution pattern for concentrations of pollutants in the vicinity of petroleum refineries.

Source Characterization

Emissions may occur from a number of sources within the refinery. Table 27 lists some of these emissions and their sources. Estimates for the volume of process unit emissions in a mode refinery are presented in Table 28.

Hydrogen Sulfide. Hydrogen sulfide is an odorous, toxic gas associated with several sources within the refinery (American Petroleum Institute 1977). It is potentially dangerous to workers because of its greater-than-air density and its tendency to paralyze the olfactory nerves, thus becoming undetectable by odor. Quantities of hydrogen sulfide may form from a number of sources within the refinery:

- o Vaporization from crude oil and raw distillates. Many sour crude oils contain quantities of hydrogen sulfide in solution that may be released.
- o Decomposition of sulfur compounds and interaction of free sulfur with hydrocarbons. Hydrogen sulfide is released from crude oil when heated, as during fractionation. Gas evolution increases with temperature and is further increased by chemical reactions among crude constituents. Sulfur compounds decompose and free sulfur reacts with hydrocarbons, yielding hydrogen sulfide. Gases driven off during distillation may contain up to 80 percent hydrogen sulfide.

TABLE 27

POTENTIAL SOURCES OF ATMOSPHERIC
EMISSIONS WITHIN REFINERIES

Type of Emission	Source
Particulates	Catalytic cracker, fluid coking, catalyst regeneration, process heaters, boilers, decoking operations, incinerators
Sulfur oxides	Sulfur recovery unit, catalytic cracking, process heaters, boilers, decoking operations, unit regenerations, treating units, flares
Nitrogen oxides	Process heaters, boilers, catalyst regeneration, flares
Hydrocarbons	Storage tanks, loading operations, water treating, catalyst regeneration, barometric condensers, process heaters, boilers, pumps, valves, blind changing, cooling towers, vacuum jets
Carbon monoxide	Catalyst regeneration, decoking, compressor engines, incinerators
Odors	Treating units, drains, tank vents, barometric condensers, sumps, oil-water separators

Source: Barrett and Goldfarb 1979.

TABLE 28
MODULE ATMOSPHERIC EMISSIONS
FROM A GASOLINE REFINERY
(lbs/day)

Process	Particulates	SO _x	CO	Hydrocarbons	NO _x
Crude distillation	3,080.0	6,400.0	533.0	533.0	5,330.0
Mid-distillate hydrotreating	45.0	64.0	38.0	65.4	518.0
Straight run naphtha hydrotreating	18.0	26.0	15.0	25.7	207.0
Heavy naphtha reformer	1,660.0	3,560.0	287.0	288.0	2,870.0
Gas oil hydrotreater	326.0	703.0	57.0	56.0	567.0
Fluid catalytic cracking	124.0	176.0	106.0	181.0	1,425.0
CO boiler	491.0	3,020.0	256.0	160.0	6,370.0
Hydrocracker	131.0	185.0	110.0	1,077.0	1,110.0
Heavy Hydrocrackate reformer	1,650.0	3,540.0	285.0	286.0	2,854.0
Propane deasphalting	622.0	884.0	48.0	81.0	656.0
Deasphalted oil hydrotreating	29.0	42.0	25.0	42.0	336.0
HF alkylation	0.4	0.6	0.4	0.7	5.0
Light ends recovery	11.0	15.0	9.2	15.7	125.0
C ₅ /C ₆ isomerization	105.0	225.0	18.5	18.2	181.0
Hydrogen plant	1,720.0	345.0	344.0	338.0	6,890.0
Storage					
Crude	---	---	---	7,550.0	---
Motor gasoline	---	---	---	5,050.0	---
Mid-distillates	---	---	---	97.0	---
Heavy fuel oil	---	---	---	Negligible	---
Sludge incineration	361.0	600.0	133.0	42.0	510.0
Tail gas treating	3.1	3,560.0	2.6	4.6	36.0
		Tail gas			
Miscellaneous	---	---	---	60,900.0	---
Total	10,380.0	22,750.0	2,270.0	76,800.0	29,990.0

Notes: Assumes a crude feed of 200,000 bbl per day.

Source: Cavanaugh 1975.

- o Evaporation from aqueous solutions, such as settled water in crude and sour distillate storage tanks. When drawn off, hydrogen sulfide gas evolves in proportion to its concentration in the solution.
- o Acidification or neutralization of caustic and amine solutions used to absorb or remove hydrogen sulfide leads to its release as a gas. Hydrogen sulfide also is released when inorganic sulfides, such as iron sulfide tank scale, are acidified.
- o Anaerobic bacterial decomposition of sulfur-containing organic materials in refinery sewer systems and stationary bodies of water release hydrogen sulfide.

Carbon Monoxide. Carbon monoxide (CO) results from the incomplete combustion of fuels. Large quantities are released during the regeneration of fluid catalytic cracking catalysts. Dry flue gases from a regenerator unit may contain 6 to 10 percent carbon monoxide, compared to 0.1 to 0.2 percent that may result from fuel combustion. Most CO is discharged hot from high stacks and, because of its less-than-air density, constitutes little hazard. CO is highly toxic and is especially hazardous when allowed to accumulate in enclosed areas.

Hydrogen Cyanide. Hydrogen cyanide (HCN), a highly toxic gas, is produced during catalytic cracking catalyst regeneration and is usually exhausted with other hot flue gases.

Sulfur Dioxide and Sulfur Oxides. Sulfur oxides, mostly sulfur dioxide (SO₂) and some sulfur trioxide (SO₃), are emitted from refineries in a quantity that is largely a function of the sulfur content of the crude oils being processed. Hazardous concentrations of SO₂ may result from the following sources:

- o Release from sulfuric acid used in processing.
- o Combustion of fuels containing sulfur compounds and the burning of coke in catalytic cracking units.
- o Disposal of sulfuric acid sludges, whether by processing in a recovery units or by direct burning in special furnaces.
- o Sulfuric acid reduction when hydrocarbons or other organic matter is oxidized, especially during the air-blowing of lubrication oils after acid treatment. Sulfur dioxide remaining in the treated oil and acid sludge may vaporize continuously under some conditions.

Thiols. Thiol or mercaptan compounds are probably the most prevalent malodorous gases released from refineries. Present in crude oil (especially sour crudes), thiols may be released from:

- o Fractionation units. Lower boiling point thiols may be released through leaks or from the jet ejectors and barometric condenser waters of vacuum distillation units.
- o Cracking units.
- o Caustic regeneration units, or steam stripping units that remove thiols to regenerate caustic solutions. Air blowing converts extracted mercaptans into less odorous organic sulfides.
- o Asphalt blowing. Thiols and other malodorous organic sulfides not removed during the air-blowing oxidation process may be a major source of refinery malodor.
- o Reactions among process stream constituents. Olefins in crude oil or formed by hydrocracking may react with sulfides to form thiols.

Phenolic Compounds. Phenolic compounds are present in large quantities in cracked distillates and some crude oils. These are usually extracted using alkaline solutions and may be released from spent caustic solutions, especially when neutralized. The presence of thiol odors, even in small concentrations, severely aggravates the obnoxious odors of phenolic compounds. Phenolic compounds may escape from process equipment in which phenols are used as extraction solvents or absorptive distillation agents, and from phenolic aqueous waste streams.

Aldehydes. Aldehydes, including formaldehyde, result from the incomplete or partial oxidation of hydrocarbons and may be found in discharged gases from asphalt air-blowing units, fluid catalytic cracking catalyst regenerating units, and from furnaces or boilers with incomplete fuel combustion.

Ammonia. Some of the ammonia used in alkaline washing solutions, for neutralizing acids, and as a refrigerant may be released. In addition, catalytic cracking may produce small amounts of ammonia.

Hydrogen Chloride. Hydrogen chloride (HCl) is an irritant gas used as an isomerization catalyst. It forms hydrochloric acid in aqueous solution. As a vapor, it may be liberated by leakage, other equipment failure, or by decomposition of catalyst sludge. The

volume of HCl used as a catalyst is relatively small and is likely to cause hazardous situations only within the refinery.

Hydrogen Fluoride. Hydrogen fluoride (HF) is an especially toxic and irritant acidic gas forming hydrofluoric acid in aqueous solution. Sources of hydrogen fluoride emissions include:

- o Leakage from HF alkylation equipment;
- o Leakage and evaporation during shutdowns;
- o Combustion of HF-containing oils from acid regeneration units;
- o Acidification or neutralization of spent HF-neutralizing agents, especially dry limestone or treated anhydrous sludge; and
- o Wastewater discharge and solid wastes containing spent caustic solutions if they are not completely neutralized.

Particulate Matter. Particulate matter is primarily emitted from process heaters and catalyst regeneration units, especially those associated with fluid catalytic cracking and reforming. These emissions are the result of combustion, except for the emission of some catalytic fines during regeneration.

Data regarding the amounts, constitutions, and sizes of refinery-generated particles are unavailable. Particulate matter may be presumed to be formed from organic compounds undergoing incomplete combustion. Various amounts and forms of PAHs, metal oxides, aldehydes, and other products of incomplete combustion or combustion of dirty fuels may be associated with particulate matter.

Organic Sulfides and Nitrogen Bases. These malodorous compounds are usually extracted with sulfuric acid when present in crude oil fractions. They may be released from acid sludges, either during acid recovery or when acid sludge is neutralized. If acid sludge and spent caustic solutions are used to neutralize each other, the resulting combined odors may be particularly nauseating and persistent even in low concentrations. Other sources of malodors are:

- o Fatty acids, soaps, and tallows used in grease manufacture;
- o Hydrogen sulfide and other organic sulfur gases used to sulfurize cutting oil;
- o Clays, earth, sorbents, filter media, and solid wastes that may release a number of obnoxious odors; and

- o Wastewater collection and processing facilities, such as separators and ponds, that may be sources of various offensive odors, especially during wet weather.

Hydrocarbon Emissions. Refineries may release considerable quantities of airborne organic compounds, mostly light-weight, volatile hydrocarbons. Federal regulations refer to these emissions as volatile organic compound (VOC) emissions. These hydrocarbons range in size and complexity from the simple alkanes to the polynuclear aromatic hydrocarbons (PAHs) and may contain elements other than carbon and hydrogen. Hydrocarbon emissions from transfer and storage facilities are discussed in the Transportation and Storage section of this report.

Considerable attention has been directed toward characterizing sources of inadvertent or fugitive hydrocarbon releases. These hydrocarbon emissions often represent constituents of marketable products, have been associated with health hazards and photochemical smog, and in high concentrations may constitute a fire or explosive hazard. Refinery hydrocarbon emissions may range from 0.1 to 0.6 percent by weight of total crude oil processed, with the lower percentage generally applicable to new facilities. Thus, a refinery processing 100,000 barrels of crude per day may release 0.5 percent, or about 500 barrels of hydrocarbons, as unintentional fugitive emissions. The composition of hydrocarbon emissions from a refinery may be expected to be a composite of all the volatile substances in the crude oil, refinery intermediates, and final products. In general, more hydrocarbons are released from refineries concentrating on producing light fractions, such as gasoline, and process units handling lighter fractions.

Fluid catalytic cracking (FCC) catalyst regeneration units may be major sources of hydrocarbon emissions. Table 29 presents concentrations of some hazardous hydrocarbons that have been identified in regenerator flue gas streams, but hydrocarbon emissions are negligible when a CO boiler, high temperature (in situ) regeneration, or other control measures are used (Barrett and Goldfarb 1979). At present, FCC-associated hydrocarbon emissions are unregulated. The high concentrations and amounts of emitted polynuclear aromatic hydrocarbons (PNAs) are of concern because many of these have been implicated as carcinogens. The concentration of benzo(a)pyrene (BAP) can be reduced to 1.41×10^{-5} kg per 1,000 bbls of feed through use of a CO boiler. PAHs and benzo(a)pyrene concentrations are unknown for flue gases from catalyst regenerators employing CO-oxidation catalysts and high-temperature regeneration (Barrett and Goldfarb 1979).

TABLE 29

HAZARDOUS HYDROCARBONS EMITTED FROM
FCC UNIT REGENERATORS

Hydrocarbons	Concentration
Aldehydes (as formaldehyde)	3-130 ppm
Cyanides (as HCN)	0.19-0.94 ppm
Phenanthrenes	400,000 ppm
Anthracene	2,070 ugr/barrel of oil charge
Pyrenes	40-28,000 ugr/barrel of oil charge
Benzo(ghi)- perylene	15-424 ugr/barrel of oil charge
Benzo(a)- pyrene	4-460 ugr/barrel of oil charge
Benzo(e)- pyrene	11-3,600 ugr/barrel of oil charge

Source: Barrett and Goldfarb 1979.

Equipment in a refinery operates at pressures ranging from less than atmospheric pressure to greater than 1,000 psig. Automatic and manual safety and pressure relief valves are necessary to permit safe discharge of excess gases, to minimize the effects of operational irregularities, and to prevent emergency situations such as fires and explosions. In the past, waste gases and liquids were routed to open pits and burned. Currently, most refineries have manifolded pressure-relief or blowdown recovery and disposal systems, usually incorporating liquid-gas separators and flares. A wide range of hydrocarbon emission types and levels may be associated with pressure-relief systems. Estimates of these emissions are not widely available.

Fugitive Hydrocarbon Emissions. Considerable attention has been paid to the release of hydrocarbons from inadvertent equipment leaks (Fernandes 1978). Pressure, heat, vibration, wear, temperature changes, and corrosion may cause leaks in valves, joints, and seals in piping and machinery. Gases, liquids, or both may leak in varying quantities, depending on the pressure, viscosity, and other factors. Testing of petroleum refinery equipment has shown that, while leaks for most equipment are not significant and are largely unavoidable, a small percentage can have high leak rates (Hustvedt and Weber 1978).

It is estimated that a typical 133,000-bbl-per-day (15,900 m³-per-day) refinery would have 27,000 potential leak sources--25,000 valves, 1,400 process drains, 250 pump seals, 14 compressor seals, and 130 relief valves (Hustvedt and Weber 1978). Nationwide, volatile organic compound emissions from equipment leaks in petroleum refineries are estimated at 170,000 metric tons per year--equal to about 1 percent of the total volatile organic compound emissions from stationary sources (Hustvedt and Weber 1978). A single leak of 1 to 10 kg per day leads to 0.4 to 3.7 metric tons of emissions per year. For comparison, a typical modern chemical plant manufacturing over 48 million pounds per year (22 kg per year) of maleic anhydride would have only about 500 potential leak sources. Most potential sources do not leak, some leak a minor amount, and a few account for a high percentage of volatile hydrocarbon release.

The distribution of leaking components in a "typical" facility is shown in Table 30 (Harrison 1978). Although the refinery-wide median leak rate is approximately 0.00035 ounces per hour (0.01 grams per hour), a small number of leaks account for a large amount of emissions (i.e., one component leaking at 3.5 ounces per hour, or 100 grams per hour, equals 10,000 leaks at 0.00035 ounces per hour.) Many other sources of fugitive emissions are transitory or area sources, such as spills and sewers. These are more difficult to quantify.

TABLE 30

DISTRIBUTIONS OF APPROXIMATE LEAK RATES
FOR TWO REFINERIES OF SIMILAR THROUGHPUT

Leak Rate	Older Refinery (%)	Newer Refinery (%)
Less than 0.10 gr/hr	96.0	98.0
0.10-6 gr/hr	2.0	0.9
6-600 gr/hr	2.0	0.7
Over 600 gr/hr	2.0	0.3
Total number of components	80,000.0	50,000.0

Source: Harison 1978.

Maintenance practices and methods of testing for leaks vary among refineries. Leak detection is complicated by the number of potential sources, their inaccessibility, and manpower and equipment requirements. Total fugitive emissions are difficult to quantify due to diffusion and dispersion above and downwind from the refinery. One method of assessing overall refinery fugitive emissions involves quantifying the distribution of hydrocarbons within a vertical transection downwind from the refinery. There is no consensus regarding the interpretation, accuracy, and reproducibility of these current methods.

Polycyclic Aromatic Hydrocarbons (PAHs). PAHs include numerous compounds that are responsible for a number of adverse effects, including: cancer of the skin, lungs, bladder, and scrotum; contact dermatitis; skin photosensitization; hyperpigmentation; acne; and folliculitis. These health effects and environmental effects of PAHs are discussed in the End Use section of this report. Refinery process streams typically contain over 5 percent four- to six-member ring PAHs, which include most PAHs associated with carcinogenic activity. These are shown in Table 31 (U.S. Environmental Protection Agency 1978).

PAHs may form from petroleum constituents by two basic reaction mechanisms: pyrosynthesis and pyrolysis. Pyrosynthesis involves the formation of PAHs from saturated hydrocarbons at high temperatures under oxygen-deficient conditions (Manahan 1975). Even low-molecular-weight hydrocarbons, including methane, may be precursors for the synthesis of PAHs. At temperatures exceeding about 930°F (500°C), carbon-hydrogen and carbon-carbon bonds are broken to form free radicals which undergo dehydrogenation and combine to form stable PAHs.

Pyrolysis involves the breaking down of large paraffinic molecules under high heat in a low-oxygen atmosphere to form less stable molecules and radicals that combine to form PAHs. PAHs readily adsorb and condense onto particulate and other surfaces and may enter the body via inhalation or percutaneous absorption.

Petroleum refineries emit considerable amounts of PAHs. Major sources are catalytic cracking catalyst regeneration units and asphalt blowing. Additional sources of refinery PAHs exposure include crude oils and the considerable amount of process furnace and boiler combustion emissions in the refinery.

PAHs are relatively large and heavy molecules, tending to remain in the residual oil and asphalt fractions during fractionation. Residual fractions may be used as a fuel within the refinery, as

TABLE 31

PETROLEUM REFINERY PROCESS STREAMS
LIKELY TO CONTAIN SIGNIFICANT
POTENTIALLY HAZARDOUS PAHs^a

Process Stream	Process Source
Atmospheric tower residuum (petroleum)	Fractionation (atmospheric)
Heavy vacuum gas oil (petroleum)	Fractionation (vacuum)
Heavy thermal cracked distillate (petroleum)	Thermal cracking
Thermal cracked residuum (petroleum)	Thermal cracking
Light paraffinic distillate solvent extract (petroleum)	Solvent extraction
Heavy paraffinic distillate solvent extract (petroleum)	Solvent extraction
Light naphthenic distillate solvent extract (petroleum)	Solvent extraction
Heavy naphthenic solvent extract (petroleum)	Solvent extraction
Hydrotreated vacuum gas oil (petroleum)	Hydrotreating
Hydrodesulfurized atmospheric tower residuum (petroleum)	Hydrotreating
Hydrodesulfurized heavy vacuum gas oil (petroleum)	Hydrotreating
Steam cracked residuum (petroleum)	Steam cracking (steam hydrocracking/ distillation)

^aFour- to six-membered condensed ring aromatics.

Source: U.S. Environmental Protection Agency 1978.

commercial fuel, as feedstock for catalytic cracking units, as asphalt for road paving, and as feedstock for manufacturing lubricating oils. Lubricating oils, food grade waxes and oils, and other more extensively refined oils generally contain few or negligible PAHs.

Fluidized Catalytic Cracking (FCC). As discussed in the processes section, FCC involves using a catalyst in the form of fine particles, fluidized or suspended in rising hot gases. Heavier crude oil fractions are broken down catalytically when passed through the catalyst bed to produce lighter aromatic fractions, highly prized for use in gasoline and as petrochemical feedstocks. In the process, a layer of coke (polymerized hydrocarbon) forms on the catalyst particles. Catalyst is regenerated by burning this off. Considerable amounts of PAHs, carbon monoxide, and other pollutants are emitted, much of these in the form of particulate emissions. Emissions estimates of hydrocarbons for FCC regenerators are listed in Table 32.

Cracking catalyst regeneration emits an estimated 6 percent of annual U.S. industrial PAHs emissions (National Academy of Sciences 1972). There were 122 refineries with fluidized-bed catalytic cracking (FCC) units with a total capacity for processing 4.7 million barrels of oil daily in 1978 (Barrett and Goldfarb 1979). Fixed-bed catalytic cracking is considered obsolete, and only three refineries employ this process. The moving-bed process is used by only 16 refineries as it is being phased out in favor of FCC. Additional FCC units are under construction, largely as replacements for older crackers or as add-ons to refineries.

New Source Performance Standards for FCC air emissions have been promulgated (Barrett and Goldfarb 1979). These rules primarily affect FCC units constructed or modified after June 1973 and call for emissions controls on particulate matter and carbon monoxide from FCC catalyst regenerators. Control measures, including electrostatic and cyclone precipitators and filters for particulate collection, and CO-boilers, which combust the CO and other organics in regenerator emissions, are implicitly required. These control measures should significantly reduce PAHs emissions and increase PAHs-laden solid waste, but data concerning this are not available.

Other Sources of PAHs. A source of some PAHs, asphalt blowing accounts for less than 1 percent of total benzo(a)pyrene industrial emissions in the U.S. (National Academy of Sciences 1972). However, it is a major source of non-combustion related PAHs emissions. Other refinery sources of PAHs may include flare systems, sludge incinerators, and process heaters.

TABLE 32

HYDROCARBONS EMITTED FROM FCC UNIT REGENERATORS

Hydrocarbons	Concentration (ppm)
Aldehydes (as H ₂ CO)	3 - 130
Cyanides (as HCN)	0.19 - 0.94
Anthracene	2,070 ^a
Pyrenes	40 - 28,000 ^a
Benzo(ghi)perylene	15 - 424 ^a
Benzo(a)pyrene	4 - 460 ^a
Benzo(e)pyrene	11 - 3,600 ^a
Phenanthrenes	400,000

^aMicrograms per barrel of oil charged.

Source: Barrett and Goldfarb 1979.

Refinery solid and liquid waste streams contain PAHs. Solid wastes for 1983 are projected to contain over 54 metric tons per year, based on 300 lbs (0.15 metric tons) per day of PAHs (Rosenberg et al. 1976). The environmental fate of refinery PAHs in solid and liquid wastes is largely unknown. Little is known about the environmental transport and effects of PAHs from solid waste, although much can be presumed to be broken down by bacteria or immobilized. Industry-wide data concerning PAHs in refinery wastewater streams are unavailable.

PAHs may pose significant health hazards to refinery workers via inhalation and skin contact. Atmospheric concentrations of various PAHs within refineries are unknown. PAHs probably condense on surfaces and pose cutaneous hazards. Simultaneous exposure to probable co-carcinogens, such as phenol and dodecanol, and irritants is likely to occur among refinery workers, perhaps exacerbating risks of cancer induction by PAHs. Photosensitization due to presumed phenanthrene exposure has been observed among asphalt blowing workers (Vandervort and Lucas 1974).

Persons residing in the vicinity of and downwind from refineries may be exposed to hazards from PAHs. Within the Los Angeles area, high average concentrations of potentially carcinogenic PAHs have been measured in the vicinity of several Long Beach petroleum refineries and chemical plants (Gordon and Bryan 1973).

Odors from Refineries. Processing units which may emit odors include catalytic cracking, asphalt production, lubricating oil treatment, and sulfur recovery units (Habib 1975). Typical sources may be vapor leakages, and crude oil and distillate vapors. The types of odors vary from sulfurous, ammoniacal, amino, phenolic, and aldehydic to those of thiols (mercaptans). Compounds emitted by refineries, their odor threshold, and odor characteristics are presented in Table 33. Hydrogen sulfide is probably the major malodorous emission from refinery operations. Other major odor emissions include aldehydes from catalyst regenerators and compressor engines, fumes from asphalt blowing, ammonia from catalyst regenerators, thiols from deodorization of gases, and sulfur oxides from incinerators, flares, boilers, and heaters. Gas freeing of storage tanks and ship compartments may provide major sources of odors. Any open stirring, venting, or flaring is liable to create odor emissions.

In the petroleum industry, absorption and combustion are the most used odor control methods and include: aldehyde absorption in bisulfite solutions; thiols absorption in sodium hydroxide solutions; hydrogen sulfide absorption in amine solutions, activated carbon, active manganese dioxide, and on sawdust; and hydrogen sulfide absorption followed by incineration or oxidation. Flares may be

TABLE 33

ODORS OF COMPOUNDS FOUND IN REFINERY EMISSIONS

Chemical	Odor Threshold (ppb)*	Odor Description
Acetic acid	1,000	Sour
Acetone	100,000	Chemical, sweet
Amine, monomethyl	21	Fishy, pungent
Amine, dimethyl	47	Fishy
Amine, trimethyl	0.2	Fishy, pungent
Ammonia	46,800	Pungent
Benzene	4,700	Solvent
Benzyl sulfide	2	Sulfidy
Carbon disulfide	210	Vegetable-like, sulfidy
Chlorine	314	Bleach, pungent
Chlorophenol	0.03	Medicinal
Dimethyl sulfide	1-2	Vegetable-like, sulfidy
Diethyl sulfide	6	Garlic-like, foul
Diphenyl sulfide	5	Burnt, rubbery
Hydrogen sulfide	5	Rotten egg
Methyl ethyl ketone	10,000	Sweet
Mercaptan, methyl	1-2	Sulfidy, decayed cabbage
Mercaptan, ethyl	0.4-1	Sulfidy, decayed cabbage
Mercaptan, n-propyl	0.7	Sulfidy
Mercaptan, n-butyl	0.7	Strong, sulfidy
Paracresol	1	Tarry, pungent
Paraxylene	470	Sweet
Phenol	47	Medicinal
Phosphine	21	Oniony, mustard
Sulfur Dioxide	470	Sharp, pungent
Toluene	2,000-4,700	Solvent, moth balls
Butane	6,000	
Heptane	18,000	
Amylenes and pentenes	170-2,100	

* Units in parts per billion by volume.

Source: Habib 1975.

associated with regeneration of caustic washing solutions to combustthiols and hydrogen sulfide. Oxygen may even be added to flares to assure complete combustion. Masking agents and odor counteractants may be used to cover up odors.

Odor emissions episodes outside the refinery tend to be sporadic, but may cause annoyance and adverse health effects in adjacent neighborhoods (Deane and Sanders 1978). Residents near several Los Angeles refineries have reported repeated annoyance with odors and some have complained of frequent or occasional dizziness, nausea, vomiting, eye irritation, burning and irritation of the nose, and other symptoms.

Refinery Contributions to Smog. Reaction mechanisms, transport, and effects of hydrocarbon-associated oxidizing smog are presented in the End Use section of this report. Approximately 85 percent of global hydrocarbon emissions originate from natural sources, mostly terpenes emitted by forests and vegetation, and methane from the bacterial decomposition of organic matter. Combustion of organic hydrocarbons, especially wood, coal, and petroleum products, contributes the major anthropogenic source of atmospheric hydrocarbon emissions. Although refinery hydrocarbon emissions account for a small percentage of global emissions, they may make significant contributions to hydrocarbon concentrations on the local and regional level.

Little information is available regarding the refinery's relative contribution to smog production. This is primarily due to: a lack of information regarding the amounts and relative proportions of constituents of refinery hydrocarbon emissions; a lack of information concerning these hydrocarbons' relative reactivities, effects, and interactions; and a lack of data concerning the environmental distribution, transformations, and fates of refinery emissions. Most available estimates of hydrocarbon emissions consider aggregate, rather than individual, hydrocarbon species emissions. Laboratory studies demonstrate a wide range in individual hydrocarbon photo-reactivities. Field atmospheric studies of smog phenomena from refinery emissions are lacking.

Many refineries are located in the vicinity of large cities that have high pollution levels and experience recurring episodes of photochemical and other atmospheric pollution. Combustion sources, usually from automobile exhaust, power generation, and industry emissions, are generally cited as the major sources of reactive hydrocarbon emissions. The relative importance of refinery hydrocarbon emissions in these localities remains largely unassessed. Refinery fugitive emissions, though largely uncharacterized, are different from those emitted by petroleum product combustion sources. The interactions among refinery fugitive emissions and other atmospheric

hydrocarbons (both natural emissions and from combustion), including the significant emissions from refinery and other combustion sources, are unknown. Refinery atmospheric emissions also contain a number of other substances that may be involved in the atmospheric chemistry of pollution: metals, nitrogen oxides, particulate matter, aldehydes, acids, amines, ammonia, and sulfur oxide compounds.

Because of difficulties involved in the real-time measurement of various concentrations of hydrocarbon emission constituents, most Federal and state regulations and activities emphasize monitoring secondary oxidants such as ozone and nitrogen oxides.

Emissions from Petrochemical Operations. Petrochemical refineries may use various process streams to produce petrochemical feedstocks and products. Although these activities are not within the scope of this report, it should be noted that in many instances such complexes are adjacent to or an integral part of refinery operations. This additional processing produces wastes and emissions besides those associated with non-petrochemical manufacturing refineries. Table 34 lists some of these processes and the wastes they produce. Distinctions between normal refinery processes and products and petrochemical-based manufacturing and processing are becoming more difficult to make as petrochemical operations become integrated with refining operations.

Air Emissions

As discussed above, petroleum refineries generate a variety of air pollutants that disperse as much as other industrial plant emissions. Information needs with respect to this subject are generic in nature, as they are also related to other facets of the oil and gas industry. These transport and transformation research needs are discussed in the Basic Effects Issues section of this report.

Water Medium

A refinery generates a variety of liquid wastes, mostly wastewaters, as a result of various processes. Major waste streams include sour water or condensates, cooling tower blowdown, boiler blowdown, storm water, ballast water, tank water bottoms, caustic scrubs, and crude desalter water (Engineering Science 1975). Most refineries apply primary and secondary wastewater treatment processes to their wastewater streams. Since it is a typical practice in refineries to collect all or several contaminated wastewater streams and combine them for treatment and disposal, it is difficult to deal with the volumes and contents of individual process-related wastewater effluent streams. Table 35 presents major process wastewater streams with qualitative indications of the contributions they make to various pollution parameters.

TABLE 34

PETROCHEMICAL PROCESSES AS WASTE SOURCES

Process	Source	Pollutants
Alkylation: ethylbenzene		Tar, hydrochloric acid, caustic soda, fuel oil
Ammonia production	Demineralization Regeneration, process condensates Furnace effluents	Acids, bases Ammonia Carbon dioxide, carbon monoxide
Aromatics recovery	Extract water Solvent purification	Aromatic hydrocarbons Solvents--sulfur dioxide, diethylene glycol
Cyanide production	Water slops	Hydrogen, cyanide, unreacted soluble hydrocarbons
Dehydrogenation Butadiene production from n-butane and butylene Ketone production	Quench waters Distillation slops	Residue gas, tars, oils, soluble hydrocarbons Hydrocarbon polymers, chlorinated hydrocarbons, glycerol, sodium chloride
Styrene from ethylbenzene	Catalyst Condensates from spray	Spent catalyst (Fe,Mg,K,Cu,Cr,Zn) Aromatic hydrocarbons, including styrene, ethylbenzene and toluene, tars
Desulfurization		Hydrogen sulfide, mercaptans

TABLE 34 (Continued)

Process	Source	Pollutants
Extraction and purification		Sulfuric acid, C ₄ hydrocarbon, caustic soda
Isobutylene	Acid and caustic wastes	Acetone, oils, C ₄ hydrocarbon, caustic soda, sulfuric acid
Butylene	Solvent and caustic wash	Heavy tars
Styrene	Still bottoms	Cuprous ammonium acetate, C ₄ hydrocarbons, oils
Butadiene absorption	Solvent	Furfural, C ₄ hydrocarbons
Extract distillation	solvent	
Halogenation (principally chlorination)		
Addition to olefins	Separator	Spent caustic
Substitution	HCl absorber, scrubber	Chlorine, hydrogen chloride, spent caustic, hydrocarbon isomers and chlorinated products, oils
Hypochlorination	Dehydrohalogenation	Dilute salt solution
	Hydrolysis	Calcium chloride, soluble organics, tars
Hydrochlorination	Surge tank	Tars, spent catalyst, alkyl halides
Hydrocarboxylation (OXO process)	Still slops	Soluble hydrocarbons, aldehydes
Hydrocyanation (for acrylonitrile, adipic acid)	Process effluents	Cyanides, organic and inorganic
Isomerization in general	Process wastes	Hydrocarbons, aliphatic, aromatic and derivative tars

TABLE 34 (Continued)

Process	Source	Pollutants
Nitration		
Paraffins		By-product aldehydes, ketones, acids, alcohols, olefins, carbon dioxide
Aromatics		Sulfuric acid, nitric acid, aromatics
Oxidation		
Ethylene oxide and glycol manufacture	Process slops	Calcium chloride, spent lime, hydrocarbon polymers, ethylene oxide, glycols, dichloride
Aldehydes, alcohols and acids from hydrocarbons	Process slops	Acetone, formaldehyde, acetaldehyde, methanol, higher alcohols, organic acids
Acids and anhydrides from aromatic oxidation	Condensates Still slops	Anhydrides, aromatics, acids Pitch
Phenol and acetone from cumene oxidation	Decanter	Formic acid, hydrocarbons
Carbon black manufacture	Cooling, quenching	Carbon black, particulates, dissolved solids
Polymerization, alkylation	Catalysts	Spent acid catalysts (phosphoric acid), aluminum chloride
Polymerization, Polyethylene	Catalysts	Chromium, nickel, cobalt, molybdenum

TABLE 34 (Concluded)

Process	Source	Pollutants
Polymerization		
Butyl rubber	Process wastes	Scrap butyl, oil, light hydrocarbons
Copolymer rubber	Process wastes	Butadiene, styrene serum, softener sludge
Nylon 66	Process wastes	Cyclohexane oxidation products, succinic acid, adipic acid, glutaric acid hexamethylene diamides, adiponitrile, acetone, methyl ethyl ketone
Sulfaction of olefins		Alcohols, polymerized hydrocarbons, sodium sulfate, ethers
Sulfonation of aromatics	Caustic wash	Spent caustic
Thermal cracking for olefin production (including fractionation and purification)	Furnace effluent and caustic treating	Acids, hydrogen sulfide, mercaptans, soluble hydrocarbons, polymerization products, spent caustic, phenolic compounds, residue gases, tars and heavy oils
Utilities	Boiler blowdown	Phosphates, lignins, heat, total dissolved solids, tannins
	Cooling system blowdown	Chromates, phosphates, algacides, heat
	Water treatment	Calcium and magnesium chlorides, sulfates, carbonates

Source: Cherimisinoff 1977.

TABLE 35

EVALUATION OF WASTEWATER FLOW AND CHARACTERISTICS

Refinery Process	Flow	BOD	COD	Phenol	Sulfide	Oil	Emulsified Oil	pH	Temp	Ammonia	Chloride	Acidity	Alkalinity	Suspended Solids
Crude oil and product storage	XX	X	XXX	X	N	XXX	XX	0	0	0	N	0	N	XX
Crude desalting	XX	XX	XX	X	XXX	X	XXX	X	XXX	XX	XXX	0	X	XXX
Crude distillation	XXX	X	X	XX	XXX	XX	XXX	X	XX	XXX	X	0	X	X
Thermal cracking	X	X	X	X	X	X	N	XX	XX	X	X	0	XX	X
Catalytic cracking	XXX	XX	XX	XXX	XXX	X	X	XXX	XX	XXX	X	0	XXX	X
Hydrocracking	X	N	N	XX	XX	N	N	N	XX	XX	N	N	N	N
Polymerization	X	X	X	0	X	X	0	X	X	X	X	0	X	X
Alkylation	XX	X	X	0	XX	X	0	XX	X	X	XX	XX	0	XX
Isomerization	X	N	N	N	N	N	N	N	N	N	N	N	N	N
Reforming	X	0	0	X	X	X	0	0	X	X	0	0	0	0
Solvent refining	X	N	X	X	0	N	X	X	0	N	N	0	X	N
Asphalt blowing	XXX	XXX	XXX	X	N	XXX	N	N	N	N	N	N	N	N
Dewaxing	X	XXX	XXX	X	0	X	0	N	N	N	N	N	N	N
Hydrotreating	X	X	X	N	XX	N	0	XX	N	XX	0	0	X	0
Drying and sweetening	XXX	XXX	X	XX	0	0	X	XX	0	X	0	X	X	XX

XXX - Major Contribution; XX - Moderate Contribution; X - Minor Contribution; 0 - No Problem; N - No Data

Source: Lebowitz et al. 1975.

It is estimated on a worldwide scale that as much oil reaches the seas from refinery and petrochemical plant effluents as from tanker and other accidents--approximately 200,000 to 300,000 tons per year (Baker 1973). For comparison, the estimated worldwide total is 1.9 million tons per year. Coastal refineries by themselves have been estimated to account for about 3.3 percent of all oil entering the ocean (National Academy of Sciences 1975).

The effects of continuous, low-level discharges of refinery effluents containing trace metals and process related chemicals not found in more common crude oil or products have received little study. Non-biodegradable effluents such as trace metals may eventually cause significant ecological damage.

Thermal pollution does not appear to be a major problem for most refineries. Cooling water is reused as much as possible for energy recovery, and when discharge is required, it likely will be passed through or added to wastewater treatment streams.

A recent review of the literature has resulted in a compilation of 370 organic substances identified in refinery effluents (Thoman and Hushon 1979). Many of these compounds are considered to be carcinogens based on animal and human tests. Others are highly toxic or pose unknown toxic hazards.

Analyses of refinery effluents have concentrated on compounds for which regulations have been implemented or proposed. These include the 129 substances on EPA's Priority Pollutant List and the parameters EPA has proposed to regulate under the Clean Water Act of 1977--parameters that include:

- o Biochemical oxygen demand (BOD);
- o Chemical oxygen demand (COD);
- o Total organic carbon, in lieu of COD;
- o Total suspended solids (TSS);
- o Oil and grease;
- o Phenolic materials;
- o Sulfides;
- o Ammonia-nitrogen;

- o Total chromium;
- o Hexavalent chromium;
- o Cadmium; and
- o Cyanides.

The presence and concentration of 129 priority pollutants and trace elements in refinery effluents have been assessed in parallel studies by EPA and the American Petroleum Institute (American Petroleum Institute 1978). The EPA study sampled intake waters, wastewater feed to biological (secondary) treatment units, and final effluent streams from 17 refineries. Concurrently, the API study sampled 9 of these 17 refineries. Samples were composites taken over a 24-hour or longer period.

Test results may be viewed as approximate rather than absolute values, as many field and laboratory factors are involved in these multiple site and laboratory sampling programs. Summaries of EPA data are presented in Tables 36 through 40. API and EPA analyses show many similarities and dissimilarities. However, several conclusions may be reached:

- o Thirty-eight of the 129 organic Priority Pollutants and 13 trace elements were identified in refineries' final effluents from combined API and EPA data.
- o Organic compounds concentrations ranged up to 2,000 ppb. Thirteen trace elements were found ranging in concentrations up to 1,000 ppb.
- o In no case were all the identified pollutants detected in any of the samples from any one refinery.
- o Biological treatment significantly reduced or removed pollutants.

The reliability and reproducibility of wastewater effluent-related analytical programs are considered inadequate by API. Disparities and anomalies in data have been identified through studies involving interlaboratory comparisons of samples, analyses of spiked samples, and duplicate analyses. EPA sampling and analysis protocols have been criticized (American Petroleum Institute 1978).

Associated with the direct discharge effluent analysis program described above, EPA sponsored a sampling program at two Los Angeles area municipal water treatment plants and refineries that contribute

TABLE 36

ORGANIC PRIORITY POLLUTANTS IN
REFINERY INTAKE WATERS^a

Compound	Frequency of Detection ^b	Concentration Range (ppb)		Number of Reported Values
		Minimum Value	Maximum Value	
Methylene chloride	5	D(<10)	G(100)	5
Chloroform	1	70	70	1
1,1,1-Trichloroethane	2	D(<10)	G(50)	2
Carbon tetrachloride	1	G(50)	G(50)	1
Trichloroethylene	1	20	20	1
1,1,2,2,-Tetrachloroethene	1	50	50	1
1,4-Dichlorobenzene	1	D(<.5)	D(<.5)	1
1,2-Dichlorobenzene	1	D(<.5)	D(<.5)	1
Naphthalene	2	1	1.8	2
Acenaphthylene	1	0.2	0.2	1
Acenaphthene	2	1.8	29	2
Fluorene	1	1	1	1
Phenanthrene/ Anthracene ^c	5	D(<.1)	160	5
Dimethylphthalate	1	20	20	1
Diethylphthalate	1	D(<10)	D(<10)	1
Fluoranthene	3	D(<.2)	29	3
Pyrene	3	D(<.1)	143	3
Di-n-butyl phthalate	4	0.2	30	4
Chrysene/Benz(a)- anthracene ^c	1	49	49	1
bis(2-Ethylhexyl) phthalate	5	110	1,100	5
Benzo(a)pyrene	1	33	33	1
Phenol	2	10	10	2

Notes: D(X) - Compound was detected at some concentration less than X, but the concentration could not be quantified.

G(X) - Greater than the value X.

^aResults are from Environmental Protection Agency data.

^bNumber of refineries where the compound was detected by one or more of the reporting laboratories.

^cCombined value for these unresolved isomers.

Source: American Petroleum Institute 1978.

TABLE 37
ORGANIC PRIORITY POLLUTANTS IN
REFINERY WASTEWATER FEEDS TO BIOTREATMENT^a

Compound	Frequency of Detection ^b	Concentration Range (ppb)		Number of Reported Values
		Minimum Value	Maximum Value	
Chloromethane	1	G(100)	G(100)	1
Bromomethane	1	D(<10)	D(<10)	1
Methylene chloride	5	10	G(100)	7
trans-1,2-Dichloroethylene	1	20	20	1
Chloroform	3	D(<5)	15	6
1,2-Dichloroethane	1	D(<10)	D(<10)	1
Bromodichloromethane	3	D(<10)	D(<10)	3
1,2-Dichloropropane	2	D(<10)	D(<10)	2
Chlorodibromomethane	1	107	107	1
Benzene	5	90	G(100)	7
1,1,2,2-Tetrachloroethene	1	G(50)	G(50)	1
Toluene	5	G(100)	G(100)	7
Ethylbenzene	5	20	G(100)	7
Acrolein	1	D(<10)	D(<10)	1
Naphthalene	8	27	1,100	11
Acenaphthylene	2	4	87	2
Acenaphthene	5	37	3,000	5
Fluorene	3	80	304	4
N-Nitrosodiphenylamine	1	D(<10)	D(<10)	1
Phenanthrene/anthracene ^c	9	0.6	1,100	13
Diethyl phthalate	1	12	12	1
Fluoranthene/Pyrene	2	20	40	3
Fluoranthene	3	2.5	8.5	3
Pyrene	6	0.7	20	7
Di-n-butyl phthalate	1	1.3	1.3	1
Chrysene/benz(a)anthracene ^c	3	6.5	50	6

TABLE 37 (Concluded)

Compound	Frequency of Detection ^b	Concentration Range (ppb)		Number of Reported Values
		Minimum Value	Maximum Value	
Chrysene	4	0.1	20	6
Bis(2-ethylhexyl) phthalate	5	50	1,100	11
Benzo(a)pyrene	1	9.5	9.5	1
Phenol	9	13	16,000	15
2,4-Dimethylphenol	4	71	750	7
p-Chloro-m-cresol	1	10	10	1
Pentachlorophenol	1	850	850	1

Notes: D(X) - Compound was detected at some concentration less than X, but the concentration could not be quantified.

G(X) - Greater than the value X.

^aResults are from Environmental Protection Agency data.

^bNumber of refineries where the compound was detected by one or more of the reporting laboratories.

^cCombined value for these unresolved isomers.

Source: American Petroleum Institute 1978.

TABLE 38
ORGANIC PRIORITY POLLUTANTS IN
REFINERY FINAL EFFLUENTS^a

Compound	Frequency of Detection ^b	Concentration Range (ppb)		Number of Reported Values
		Minimum Value	Maximum Value	
Methylene chloride	4	D(<10)	60	4
Chloroform	1	D(<5)	D(<5)	1
Benzene	1	6	6	1
1,1,2,2-Tetra- chloroethene	1	D(<10)	D(<10)	1
Toluene	1	35	35	1
Naphthalene	1	0.1	0.1	1
Acenaphthene	1	6	6	1
Phenanthrene/ anthracene ^c	2	0.8	D(<10)	2
Dimethylphthalate	1	3	3	1
Diethylphthalate	2	D(<10)	30	2
Fluoranthene	1	D(<.1)	D(<.1)	1
Pyrene	3	D(<.1)	7	3
Chrysene/benz anthracene ^c	1	0.8	0.8	1
Chrysene	3	D(<.1)	1.4	3
Bis(2-ethylhexyl) phthalate	5	190	2,000	5
Benzo(a)pyrene	2	1.3	2.9	2

Notes: D(X) - Compound was detected at some concentration less than X, but the concentration could not be quantified.

G(X) - Greater than the value X.

^aResults are from Environmental Protection Agency data.

^bNumber of refineries where the compound was detected by one or more of the reporting laboratories.

^cCombined value for these unresolved isomers.

Source: American Petroleum Institute 1978.

TABLE 39

FREQUENCY AND CONCENTRATION RANGE OF
TRACE ELEMENTS IN REFINERY INTAKE WATERS^a

Element	Frequency of Detection ^b	Concentration Range (ppb)		Number of Reported Values
		Minimum Value	Maximum Value	
Zinc	15	15.0	120	15
Chromium	13	1.0	60	13
Copper	10	1.0	210	10
Lead	8	1.0	40	8
Antimony	1	1.0	1	1
Thallium	1	3.0	3	1
Nickel	5	1.0	58	5
Arsenic	5	3.0	27	5
Selenium	6	2.0	13	11
Cadmium	1	2.0	2	1
Mercury	5	0.1	6	13

^a Results are from Environmental Protection Agency data.

^b Number of refineries where the element was detected by one or more of the reporting laboratories.

Source: American Petroleum Institute 1978.

TABLE 40

FREQUENCY AND CONCENTRATION RANGE OF
TRACE ELEMENTS IN REFINERY FINAL EFFLUENTS^a

Element	Frequency of Detection ^b	Concentration Range (ppb)		Number of Reported Values
		Minimum Value	Maximum Value	
Zinc	16	25.0	700	22
Chromium	15	1.0	1,000	18
Copper	10	3.0	180	10
Lead	5	2.0	58	8
Antimony	3	1.0	370	3
Thallium	2	3.0	12	5
Nickel	5	3.0	58	8
Arsenic	4	5.0	900	7
Selenium	7	3.0	32	21
Silver	1	15.0	15	1
Cadmium	2	1.0	5	2
Mercury	5	0.5	6	10

^a Results are from Environmental Protection Agency data.

^b Number of refineries where the element was detected by one or more of the reporting laboratories.

Source: American Petroleum Institute 1978.

their wastewaters to these plants. The results show that secondary biological treatment by publicly owned treatment works (POTWs), involving the treatment of refinery wastes by municipal wastewater treatment facilities, reduced concentrations of pollutants to levels similar to those achieved by on-site refinery secondary treatment.

In 1977, EPA conducted the 1977 EPA Petroleum Refining Industry Survey. Three mailings were made to obtain and verify data from each refinery in the U.S. Included in the survey were questions regarding wastewater flows, priority pollutant chemicals purchased and manufactured, and analyses of wastewaters. Seventy-one toxic (priority) pollutants were listed as being purchased as raw or intermediate materials, as indicated in Table 6. At least 10 percent of U.S. refineries purchased the following compounds: benzene, carbon tetrachloride, 1,1,1-trichloroethane, phenol, toluene, and zinc, chromium, copper, and lead compounds. Zinc and chromium compounds were purchased by 28 percent, and lead compounds (probably gasoline additives) were purchased by nearly 48 percent of the refineries. Forty-five toxic pollutants were manufactured as intermediate or final products, while at least 10 percent of the refineries manufactured benzene, ethylbenzene, phenol, and toluene. The purchase, manufacture, and use of these chemicals may be more relevant to workers' health than to wastewater effluent hazards.

Based on the information gathering activities summarized above and other information, EPA has proposed limitations on refinery effluent discharges into U.S. waters and into publicly owned treatment works (U.S. Environmental Protection Agency 1980b). Levels of treatment technologies and timetables for proposed refinery effluent treatment requirements are shown in Table 41. EPA has proposed controlling effluent levels of chromium (both total and hexavalent), phenolic compounds, oil and grease, total suspended solids, biochemical oxygen demand (BOD), ammonia (nitrogen), sulfides, and effluent pH from several classes of refineries. The current and future implementation and effects of effluent limitations are difficult to assess. Ultimately, the goal is to eliminate wastewater discharges (Level VI of abatement technology in 1985; Table 41). This would be accomplished by treating wastewaters for reuse, which would have a strong impact on the amount and types of solid wastes that refineries generate.

Summary of Research Needs

Basic research needs related to refinery air and water effluent emissions, but also relevant to other facets of the oil and gas industry, are discussed in the Basic Effects Issues section of this report. The following are selected research issues relating primarily to refineries.

TABLE 41
SUMMARY OF ABATEMENT LEVEL TECHNOLOGY

Technology	Level PT Pretreatment and in-Plant Control	Level I Secondary Treatment	Level II Advanced Secondary Treatment	Level III Advanced Secondary Treatment	Level IV Advanced Tertiary Treatment	Level V Advanced Tertiary Treatment	Level VI Zero Discharge	Level T-1 ^a Toxic Metals Reduction	Level T-2 ^a Cyanide Reduction
Associated year of implementation	1977	1977	1977	1977	1983	1983	1985	--	--
Equivalent EPA guideline technology	--	--	BPCTCA	BADT ^b (NSPS)	BATEA	--	EDOP	--	--
Gravity oil/solids removal (API or CPI separators)	X	X	X	X	X	X	X	--	--
Secondary oil/solids removal (dissolved air flotation or granular media filtration)	X	X	X	X	X	X	X	--	--
Roughing biotreater (trickling filters or rotating bio- logical con- tractors)	--	--	--	--	Option 2	Option 2	--	--	--

TABLE 4- (Continued)

Technology	Level PT Pretreatment and in-Plant Control	Level I Secondary Treatment	Level II Advanced Secondary Treatment	Level III Advanced Secondary Treatment	Level IV Advanced Tertiary Treatment	Level V Advanced Tertiary Treatment	Level VI Zero Discharge	Level T-1 ^a Toxic Metals Reduction	Level T-2 ^a Cyanide Reduction
High efficiency bioreactor (aerated lagoons or activated sludge with clarifiers)	--	X	X	X	Option 1	Option 1	X	--	--
Tertiary oil/solids removal (mixed- media fil- tration)	--	--	X	X	X	X	X	--	--
Treated wastewater reuse (reuse of treated process wastewater to reduce total effluent dis- charge)	--	--	--	X	X	X	X	--	--
Activated carbon adsorption	--	--	--	--	X	X	X	--	--

TABLE 41 (Concluded)

Technology	Level PT Pretreatment and in-Plant Control	Level I Secondary Treatment	Level II Advanced Secondary Treatment	Level III Advanced Secondary Treatment	Level IV Advanced Tertiary Treatment	Level V Advanced Tertiary Treatment	Level VI Zero Discharge	Level T-1 ^a Toxic Metals Reduction	Level T-2 ^a Cyanide Reduction
Dissolved salts removal (reverse osmosis, ion ex- change, freeze crystallization, evaporation)	--	--	--	--	--	X ^c	X	--	--
Chemical pre- cipitation and sedimentation	--	--	--	--	--	--	--	X	--
Alkaline chlorin- ation or electrolysis	--	--	--	--	--	--	--	--	X

Notes: X Represents an applicable regulation.

-- Represents not an applicable regulation.

^aThese are add-on systems for all abatement levels.

^bBADT (NSPS) is equivalent to Level II end-of-pipe treatment with Level III in-plant control.

^cFifty percent of wastewater flow.

Source: Sittig 1978.

Acid Rain. Considerable research is directed toward defining and resolving issues associated with acid rain. This problem has primarily been attributed to the product of a series of complex chemical reactions in which sulfur and nitrogen oxides, resulting from the combustion of coal and oil, combine in the atmosphere to form acids, which can return to earth as components of rain or snow.

Currently, collected data are beginning to show that agents other than sulfur and nitrogen (e.g., halogens and metals), present in the precipitation may contribute to biological effects on terrestrial and aquatic biota. Certain gases released from refineries may play a role in the formation or effects of acid rain, at least on a local scale.

Hydrogen chloride, released as a gas from refineries, forms hydrochloric acid in an aqueous solution. Hydrogen fluoride, also released as a gas, forms hydrofluoric acid in an aqueous solution. Releases of formaldehyde, metals, ammonia, and sulfates from refineries can contribute to the formation of precipitation that can be detrimental to biota. This problem should be explored with respect to its pervasive characteristics, especially on a local scale.

Toxic Hydrocarbon Emissions. A comprehensive and detailed source characterization study is needed to determine, both qualitatively and quantitatively, the nature and extent of constituents of airborne refinery emissions that are potential carcinogens, mutagens, teratogens, or reproductive hazards. This study should focus on unit processes and include fugitive emissions from leaks, spills, and liquid and solid waste disposal. The study also should include emissions in the form of gases, vapors, particles, and condensates on refinery equipment.

Toxic Hydrocarbon Effluents. A comprehensive and detailed source characterization study (similar to the one described above) is needed with respect to liquid refinery effluents. Low-level hydrocarbon discharges of potential carcinogens should be quantified. This study should be a follow-up to a recent study which identified 370 organic substances in refinery effluents (Thoman and Hushon 1979).

Precision and Reproducibility of Analyses. Analyses should be standardized and made reliable, especially with regard to the detection and measurement of organic compounds, notably potential carcinogens existent in low concentrations in refinery waters. The disparities and anomalies, as cited by the American Petroleum Institute, with respect to interlaboratory comparisons of samples, analyses of spiked samples, and duplicate analyses, should be

resolved through the development and implementation of quality assurance procedures. New data should be collected utilizing these procedures.

Characterization of Refinery Wastes and Emissions. Refinery emissions and wastes are complex mixtures. These require more industry-wide analysis and characterization. Toxic effects from these mixtures require study.

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Part 5

Liquefied Energy Gases

LIQUEFIED ENERGY GASES SUMMARY

A great deal of controversy has surrounded the liquefied energy gas industry, particularly the liquefied natural gas (LNG) industry, for several decades. Many relevant studies have been conducted, although a total, integrated study of the entire industry has not been performed. A well structured and rigorous risk assessment is needed which would deal comprehensively with current and projected LNG imports, domestic production, LNG transportation and handling operations and movement patterns, and the probability of sabotage.

Cooling water discharges from liquefaction facilities are an environmental problem. Research should be directed toward the following areas: finding beneficial uses for the waste heat, determining the capacity of aquatic biota to assimilate biocides and other cooling water additives, and evaluating the use of air as a heat sink.

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LIQUEFIED ENERGY GASES

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LIQUEFIED ENERGY GASES

TECHNOLOGY DESCRIPTION

This section primarily addresses the processing and handling of liquefied natural gas (LNG) and liquefied petroleum gas (LPG). These substances are commonly stored and handled with the use of cryogenic temperatures. Propane (a major LPG) can also be stored as a liquid under pressure without refrigeration or with only moderate refrigeration, but this is not the case with LNG. Naphtha, another liquefied gas, can be stored as a liquid at near atmospheric temperature and pressure.

Another group of hydrocarbons, the natural gas liquids, (NGL), are also discussed in this section. These include liquid propane and other compounds and mixtures. These hydrocarbons are usually transported and stored as liquids. (Except for LNG, all other hydrocarbons discussed in this section can exist in the liquid state through the application of pressure or moderate refrigeration.)

Types of Gases

Liquefied energy gases (LEG) are hydrocarbon gases converted to a liquid state by pressure and cooling. The liquefied state may reduce their gaseous volume by hundreds of times and allows for efficiency in storage and handling (Figure 1). One cubic meter of LNG will form about 12,000 cubic meters of a flammable natural gas-air mixture and 1 cubic meter of LPG will form a slightly larger volume of a flammable gas-air mixture. Naphtha, a less hazardous group of heavier hydrocarbons, is transported and stored as a liquid at near atmospheric temperature and pressure. Currently, liquefied energy gases (imported LNG, LPG, and naphtha derived from crude oil) comprise about 3 percent of the energy used in the U.S. and are used to supplement domestic supplies of natural gas. About 2 percent of the nation's energy is supplied by LPG, primarily propane (General Accounting Office 1978).

When cooled to -260°F , natural gas becomes a liquid about 1/600th of its volume at normal atmospheric temperature and pressure. Thus, a storage tank of LNG contains 600 times more energy than an identical tank containing natural gas. LPG liquefies at -44°F as propane and -310°F as butane. LPG also liquefies under pressure at atmospheric temperature (see the History of Natural Gas Liquids, below in this section of the report).

FIGURE 1
TYPICAL FLOW PLAN FOR LIQUEFIED ENERGY GASES

Although accounting for the majority of LEG usage, LPG has received much less public attention than the relatively new LNG industry. LPG and naphtha have been used for many years as feedstocks for petrochemicals. In 1976, 13 million customers, mostly in rural areas, used LPG as an energy source. Naphtha has been a major source of jet fuel and it is used in the production of synthetic natural gas (SNG). The SNG is pipeline quality gas, of almost pure methane, and is synthesized from naphtha by the sequential processes of sulfur removal, catalytic gasification, methanation, and carbon dioxide and water removal.

Although LNG has been used as a form for the storage of domestic natural gas since the early 1940s, recently it has been imported in ships. These imports, which supplied less than 1/10th of 1 percent of U.S. natural gas demand in 1978, could supply up to 15 percent by 1985 (Office of Technology Assessment 1977), posing additional problems with respect to national dependence upon foreign sources of fossil fuel.

NGL are heavier hydrocarbon mixtures recovered in conjunction with oil and gas production and at natural gas processing plants (Figure 2). These liquids are gaseous in underground reservoirs, but they are also recoverable in liquid form by condensation, absorption, and adsorption within surface equipment and at natural gas processing plants. In addition, they accumulate as liquid products of petroleum refining. Natural gas liquids are considered a supplemental rather than an alternative hydrocarbon resource (U.S. Department of the Interior 1970).

The mixtures of gaseous compounds within the paraffin hydrocarbon series, from which liquid products are recovered, are divided into four broad categories: LPG, liquefied refinery gas (LRG), natural gasoline, and condensate.* As a natural gas liquid, LPG is mostly propane or butane or mixtures of both compounds which are maintained in a liquid state under pressure. LRG is liquefied propane or butane produced by a crude oil refinery. It differs from LPG in that propylene and butylene may be present due to various chemical reactions within the refinery. Natural gasoline refers to liquid hydrocarbon mixtures containing quantities of pentanes and heavier hydrocarbons which have been extracted in a natural gas

*Condensate is the liquid formed by the condensation of a vapor or gas; especially the hydrocarbon liquid separated from natural gas, which because of changes in temperature and pressure, condenses when the gas from the field reservoir is delivered to the surface separators and which remains liquid at atmospheric temperature and pressure.

FIGURE 2
SCHEMATIC FLOW CHART OF CRUDE OIL, NATURAL GAS, AND
NATURAL GAS LIQUIDS

processing plant from gases and liquids that remain after previous separation of liquid containing condensate or crude oil.

History of LNG

Since 1960 the LNG industry has undergone rapid growth, primarily because of an increase in its use in peak-shaving, i.e., supplying fuel gas for distribution from an auxiliary storage source during periods of maximum demand when the primary source is not adequate. Peak-shaving has played an important role in meeting peak demands for natural gas in New England and the South Atlantic states. There are now about 64 U.S. peak-shaving plants in operation and 2 more are expected to begin operation by the end of 1982 (Scorecard 1980).

Recently, LNG has also been imported to meet baseload needs. Currently baseload LNG is imported from Algeria and is received and gasified at three East Coast marine terminals: Everett, Massachusetts; Cove Point, Maryland; and Elba Island, Georgia. One new LNG terminal is under construction in Lake Charles, Louisiana, and three are planned for Little Cojo, California; Ingleside, Texas; and Port O'Connor, Texas (Hale 1980; Scorecard 1980).

Currently, one domestic baseload LNG liquefaction facility with ancillary marine terminal facilities is in operation. Located at Kenai, Alaska, it began operations in 1969 with the first commercial shipment of LNG ever exported from North America and also with the first LNG ever imported into Japan. Another baseload LNG liquefaction facility is expected to begin operation in Cook Inlet, Alaska, in 1982 (Scorecard 1980).

Many scenarios exist for the projected dependence of the U.S. on LNG imports. These vary from a modest increase of 1.5 times the present level that would take place with an extension of the past 20-year trend, to almost a fivefold increase by the year 2000. The future of LNG imports will be influenced markedly by the size of recoverable gas reserves within the exporting countries, the political pressures exerted by exporting countries in the form of production curtailments and price increases, and national concern over the U.S. balance of payments. Methane and similar gases produced from domestic fossil based synthetic fuels and biomass may shift in the LEG industry from imports to domestic baseload and peak-shaving storage facilities.

History of NGL*

In 1903, years before the first commercial extraction of natural gasoline, hydrocarbon liquid accumulations were accidentally observed

*Taken largely from U.S. Department of the Interior 1970.

in field gathering lines of natural gas pipelines. In such instances, the natural gas in the line had been collected from casingheads (space between the tubing and casing in oil wells), and the recovered liquids were called casinghead gasoline. Later, as other gas sources were developed, the term casinghead gasoline became a misnomer and the term natural gasoline evolved.

Between 1908 and 1910, billions of cubic feet of gas became available for extraction. When gas processors began to compress natural gas to higher pressures, they discovered that higher NGL yields were obtained than at lower pressures. This was the first compression method developed for collecting NGL.

Throughout the first half of the 20th century, gas processors blended natural gasoline with purchased naphthas to raise gasoline quality, making the product competitive with refinery gasoline. Soon the refiners began using a greater portion of their naphthas in gasoline refining, making blending stocks scarce to gas processors. At the same time, oil refineries required a gasoline product with high API gravity to add volatility to their products; therefore, natural gasoline became a vital ingredient of standard gasoline to meet quality specifications. This trade-off reduced the competitive relationships between naphtha and natural gasoline.

Despite the rapid growth of the early compression plants, and their ability to process richer gas streams, they were inefficient and not amenable to processing the leaner natural gas.

The early natural gas compression plants were called gasoline plants because most of their output was natural gasoline. They were built in the absence of marketing surveys or economic analyses, and relied upon days' payout (time required for net income to equal initial investment). Processors selected plant locations primarily on the basis of adequacy of gas supply and open marketing.

Following World War II, available steel and advances in electrical welding technology permitted the use of high-carbon steel in pipe making and manufacturing and allowed the construction of larger-diameter pipelines. This development, coupled with increased demand for natural gas, shifted the fuel supply in the Southwest from oil to gas. Long-distance gas pipelines were extended from the Southwest to the West Coast, the Midwest, and the East Coast. As an outgrowth of this expansion, natural gas processing plants were constructed to meet the rapidly increasing demand for both natural gas and natural gas liquids.

In the early 1940s a trend toward joint ownership of processing plants had begun. Joint operations made it feasible for a group of operators to finance larger plants to meet changing demand. Gas cycling recovery from select unitized petroleum reservoirs was found to be ideally suited for this purpose. Cycling permits royalty owners and leaseholders to obtain a present return on their mineral rights through production of NGL rather than to defer returns until the future when markets exist for residual gas. During the 1940s, propane and butane were consumed in ever-increasing quantities as a raw material for petrochemical plants and to meet the demand for domestic bottled gas.

In the late 1950s significant technological advances permitted the storage of natural gas liquids in salt domes along the Gulf Coast, which helped overcome price instability and offered a means for supplying the wide seasonal variations in markets. More recently, economical methods for storing liquids have been extended to apply to depleted oil and gas reservoirs, salt water sands, shale deposits, mined caverns, frozen earth, and aboveground refrigerated storage.

Within the last two decades marked refinements in technology have accompanied a high rate of growth in production. Higher recoveries of plant concentrations of ethane and propane have coincided with increased automation and the construction of refrigeration processing plants located adjacent to markets. New liquid hydrocarbon supplies have emerged as the petroleum industry has expanded to offshore operations in Louisiana and Alaska.

Domestic production of natural gas liquids from gas processing plants in 1976 was about 587 million barrels, or 1.5 percent less than in 1975.* The year 1976 represented the fourth consecutive annual decline in production, which was attributed to a decline in the availability of supplies of natural gas and to a decrease in the liquid content of the gas being processed. Production at gas processing plants has been variable since 1976. In 1979, production was about 615 million barrels (U.S. Department of the Interior 1978; U.S. Department of Energy 1979).

*Because of the complexity of the petroleum and natural gas industry and the absence of accepted definitions pinpointing the phase of extraction or separation, numerous reporting sources have used different systems of classifying and measuring production data over the years. This has created inconsistencies in the reported data. Data in this section should be used in this light and is presented only as an indicator of general industry trends.

Domestic demand for production at refineries in 1976, excluding that blended into other products at refineries or terminals, increased 5.1 percent over 1975. Increases since 1976 have averaged 3 percent or less.

Total natural gas liquids have increased at a fairly constant rate since 1950. In millions of barrels per year, the approximate growth has been: 1950, 182; 1960, 340; 1970, 600; and 1979, 752. From 1950 to 1970, natural gas liquids increased from 6 percent to over 11 percent of the total U.S. liquid hydrocarbon supply.

LEG Processes

Liquefaction

The two principal methods used for liquefaction are the cascade cycle and the expander cycle. The cascade cycle uses a series of refrigerants to sequentially lower the temperature. The refrigerants are usually liquid propane or ammonia, ethane or ethylene, and methane. Usually propane is used first to decrease the temperature to about -31°F to -44°F . The second stage uses ethane or ethylene to decrease the temperature further to about -142°F to -148°F . The final stage reduces the temperature to at least -258°F by means of methane-cooled heat exchangers (Figure 3).

The expander cycle is based on the concept of self-refrigeration as gas expands during a large pressure drop. When compressed gas passes through an engine it expands, resulting in a lowering of the temperature of the gas. Multiple refrigerants are not used. This method of liquefaction is ideal for use in peak-shaving plants at the end of high pressure transmission lines where a large volume of gas needs to be depressurized before entering distribution mains (Figure 4). It is not as useful for baseload export-import systems.

Prior to liquefaction, gas cleaning is needed to remove water, carbon dioxide, hydrogen sulfide, lubricating oils, odorants, and dust. These contaminants solidify at low temperatures and must be removed to avoid clogging of liquefaction, regasification, and transmission equipment (American Gas Association 1973).

LEG Marine Terminals

A refrigerated LEG marine terminal can serve as a dispensing or receiving depot serving oceanic tankers or barges that transship LEG cargo via inland waterways. Due to high unloading rates from tankers (off-loaded in 20 hours or less), it may not be economically practical for marine terminals to store substantial amounts of LEG at any temperature and pressure different from the storage conditions aboard ship.

Source: Adapted from American Gas Association 1973.

FIGURE 3
CASCADE CYCLE FOR THE LIQUEFACTION OF NATURAL GAS

Source: Adapted from American Gas Association 1973.

FIGURE 4
EXPANDER CYCLE FOR THE LIQUEFACTION OF NATURAL GAS

The relative costs of storage under pressure and refrigeration for natural gas and propane are shown in Table 1. The data are for land storage, but also are representative for storage on ships. LPG can be stored under pressure with a relatively low level of refrigeration, but this is not true for LNG.

LEG Storage and Handling

LNG usually is stored in aboveground, double-walled metal tanks prior to transfer to tankers or to regasification facilities. One type of storage tank can contain up to 65,000 gallons, and can operate at pressures between 50 and 250 psig (pounds per square inch as observed on a gauge). The inner wall is composed of a material capable of withstanding cryogenic temperatures and the outer wall is usually constructed of carbon steel. The space between the inner and outer wall contains a partial vacuum and may be filled with perlite or urethane.

In another type of storage tank, capable of containing up to 1.2 million gallons, LNG is stored at atmospheric pressure. The space between the inner and outer walls may be filled with insulation in a dry, inert atmosphere. In a variation of this type of tank, a suspended and insulated ceiling eliminates the need for a roof composed of cryogenic materials. The capacity of these modified tanks is up to 24 million gallons (U.S. Environmental Protection Agency 1977).

Several pre-stressed concrete storage tanks are in service. A 13.2-million-gallon tank surrounded by an earthen berm is in service on Staten Island, New York. There, a heating cable is located below the concrete floor to prevent the upthrust of ground caused by moist soil freezing (frost heaves). Others in operation are located at Yarmouth, Massachusetts, on Cape Cod (2.2 million gallons), Massachusetts, and in Cumberland, Rhode Island (1.1 million gallons).

Other storage techniques, such as frozen holes or pits in the earth and mined caverns, have been tested or investigated in the U.S. and have been found not to be feasible because excessive heat leaks lead to a high rate of boil-off, frost heaves, or other problems. However, an 11.3-million-gallon inground storage unit is located in Arzew, Algeria, and four 13.2-million-gallon units are on Cagney Island, England. These units are being phased out of service.

In transfer operations between ship and onshore storage, sufficient interlocks must be provided to prevent overpressuring or overfilling storage tanks. Emergency shutdown measures must be available to terminate filling if abnormal conditions develop. Fill rates may

TABLE 1
CONDITIONS OF CONTAINMENT

Product	Pressure				Fully Refrigerated Storage			
	Pressure	Product (lbs/ft ³)	Vessel (lbs/lb of product)	Cost (per lb of product)	Pressure	Product (lbs/ft ³)	Vessel (lbs/lb of product)	Cost (per lb of product)
Natural gas	Pressure storage not feasible				1 psig	29.3	0.098	6.70¢
Propane	250 psig	27.7	0.29	25.7¢	1 psig	36.6	0.058	2.32¢

Notes: Costs in 1972 dollars.

Comparisons are for 20,000 tons of product.

psig = pounds per square inch above atmospheric pressure (as read by a gauge).

Source: Adapted from Clapp and Litzinger 1972.

vary from a few hundred to tens of thousands of gallons per minute. High volume fill rates can result in large quantities of vapor being displaced from an onshore storage tank. Ship pump energy also may create a large volume of vapor. Vaporization can occur from the heat of the ship and fill lines. Such heat loss generally is controlled through the use of insulation. Vapors formed during handling may be refrigerated, vented, flared, or returned from a storage tank to the off-loading tanker to replace the evacuated space within on-board tanks.

For LPG, it usually is economical to use only a minimal amount of insulation in the construction of storage tanks and to provide a refrigeration system capable of reliquefying the boil-off gas. An LPG boil-off vapor reliquefaction cycle may consist of several stages of compression and the rejection of latent heat to the atmosphere and may utilize an air-cooled condenser. The resultant high-pressure liquid is flashed into the relatively low pressure and temperature environment of the storage tank. Pressurized storage is another alternative for storing LPG. Under these conditions, LPG stored at -10°F and warmer is more often placed in single-walled tanks. For temperatures colder than -10°F , LPG tanks are either double-walled or single-walled, depending on construction costs, operating and extra refrigeration costs, maintenance and longevity of insulation, and safety (Clapp and Litzinger 1972).

The reliquefaction of LNG boil-off vapors is more expensive and also undesirable because of the need to maintain a positive pressure of an atmosphere saturated with boil-off vapors within a storage tank to avoid the formation of an atmosphere susceptible to combustion. For these reasons, LNG tanks are heavily insulated and only small amounts of boil-off gas are compressed and sent to a distribution system. A portion of the boil-off gas may be reliquefied.

About 85 percent of LPG is stored under pressure in underground salt domes or mined caverns. Some is stored in relatively small aboveground tanks. As of 1978, only 23,000 cubic meters of LPG was stored aboveground and distributed among 20 storage facilities (General Accounting Office 1978).

LEG Transportation

Domestic transportation of LPG is mostly by high-pressure pipeline (70,000 miles). The remainder is transported by rail cars (16,000, mostly uninsulated with a capacity of 700 barrels per car) and highway vehicles (25,000). A large LPG tank truck, usually a tractor-trailer combination, can hold about 250 barrels. Refrigerated barges with capacities of up to 16,000 barrels are used for transporting LPG and anhydrous ammonia in cylindrical tanks

approximately 16 feet in diameter and 240 feet long (General Accounting Office 1978; Tiratsoo 1979).

For over two decades, LPG has been successfully transported by sea from the Middle East to North America, Japan, and Western Europe. The early, low-tonnage vessels carried LPG under pressure in heavy cylindrical tanks in their holds and were limited to a carrying capacity of 3,800 barrels by the difficulty of manufacturing and installing suitable tanks (Tiratsoo 1979).

With time it was determined that refrigerated LPG could be handled more economically at atmospheric pressure than if liquefaction had to be maintained under pressure. Thus, in 1959 the first semi-refrigerated LPG carrier was constructed and 2 years later it was put into service. It was used to carry butane and had a capacity of 64,500 barrels, maintained at atmospheric pressure. (Tiratsoo 1979).

The largest of today's LPG tank ships holds about 629,000 barrels (about 60 percent of the capacity of the largest LNG carriers). Currently, 10 major LPG import terminals are operating.

Due to the high costs of insulation and refrigeration, LNG is usually stored and regasified before it is transported by pipeline. Only about 75 LNG tanker-trailers, each about 40 feet long and with a capacity of about 250 barrels, are available for transporting LNG to small or remote gas companies where it is regasified. A "thermos bottle" design is used which includes an aluminium inner shell vacuum insulated from a steel outer shell. The evacuated space between the walls is filled with perlite. Unloading is carried out by pressurizing the gas space in the top of the tanker to about two atmospheres using revaporized gas (General Accounting Office 1978; Tiratsoo 1979).

The first barge built especially to transport LNG in shallow waterways was the 297-foot-long Massachusetts, commissioned in 1973 for the Distrigas Corporation. It has been used to carry LNG between U.S. Gulf Coast terminals in 320,000-barrel loads contained in four insulated aluminum tanks (Tiratsoo 1979).

The transportation of LNG is essentially, by volume, restricted to the marine environment. Since 1964 when the first tankers were put into service, tanker capacities have risen from 27,400 cubic meters to over 165,000 cubic meters. LNG tankers are double-hulled and have insulated cargo tanks constructed with cryogenic materials. The LNG tanks are freestanding and anchored in the hull or to the deck of the ship. They are comprised of a membrane that is supported by insulation lining the hull, or forms a structural part of the

ship's hull. Tanker engines can use either boil-off from the cargo or conventional fuel. Boil-off gas is always available because a portion of the LNG load is kept on board to keep the tanks cold (General Accounting Office 1978; University of Oklahoma 1975).

Regasification of LNG

LNG regasification facilities vaporize the liquid by passing it through heat exchangers. These are heated by air or water at ambient temperature, which may be raised in the winter by the heat of fuel combustion or by the gas itself. Regasification occurs at pressures of up to 1,200 psig, which are sufficient for input of the gas into a conventional natural gas pipeline.

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HEALTH AND ENVIRONMENTAL EFFECTS

The salient health and environmental issues associated with liquefied energy gases are discussed in this section. The information is categorized by problem area.

Occupational Health and Safety

In cryogenic LEG facilities, several types of health and safety hazards can exist. Insulation failures and escaping LNG, vapor, or refrigerants present the possibility of cryogenic burns from contact with cold liquid, vapor, or surfaces. The severity of the burn would depend upon length of exposure, temperature of the source, and the rate of heat transfer. If the skin has surface moisture, it may freeze onto the cold object. Skin may adhere to the cold surface when the affected area is removed.

Prolonged exposure to cryogenic temperatures also results in hypothermia--a decrease in body temperature. At a lower body temperature, physical and mental capabilities are greatly reduced and death usually occurs at a body temperature below 80.5°F.

Vapors are not toxic, but they hug the ground and exclude oxygen to the point that asphyxiation occurs. This may occur so slowly that the victim realizes the danger too late to save himself. These hazards, under normal conditions, are limited to the boundaries of an LNG facility.

LNG workers are protected, to an extent, by safety glasses or goggles, non-conductive fire-resistant hard hats, and protective clothing, gloves, and shoes. These items are fallible, however. Temperature cycling and sudden drops in temperature can create thermal stresses and lead to material weakening and possible failure unless vaporization takes place at a constant rate.

Public Health and Safety

LNG Spills*

Major LNG spills (i.e., those considered to have the greatest potential for harm) may result from groundings, failures of the integrity of storage tanks, and collisions at sea involving an LNG tanker. Minor spills can occur when released refrigerants and solids block a pipeline during or after liquefaction. They can also result from malfunctions on board tankers, leaks in the transportation system linking an LNG tanker to onshore storage areas, and accidents

*Taken largely from U.S. Environmental Protection Agency 1977.

during maintenance. Thus, an LNG spill may occur on land or water, and even underwater in the case of a submerged tanker. The consequences of these events are substantially different.

If LNG is spilled on the ground, it begins to boil violently and vaporize. If the spill continues, a pool forms; it freezes the ground underneath, and the boiling rate becomes constant. If LNG spills on water, it is usually unconfined, which allows it to spread rapidly and continue to boil at a high rate. An ice layer will form under an unconfined spill. As this layer thickens, the rate of heat transfer is reduced and the boiling rate is reduced.

Spilled LNG will either ignite immediately or form a low-lying vapor cloud. Such a cloud will be denser than air (up to a temperature of -40°F) and will hover above the ground or water. The vapor generation rate is proportional to the pool area and the vapor cloud can be cigar or pancake shaped. It will begin to rise when it is warmed sufficiently and its density approaches that of air. The cloud will either eventually dissipate or be driven by the wind as a plume. The distance a plume can travel before it falls below the lower flammable limit (LFL) depends on meteorological conditions. Estimates range from 1 to 50 miles. Until the LFL is reached, ignition may occur at any time and involve flashbacks to the original pool. For LNG to ignite, it must form a 5 to 15 percent mixture with air and an energy source (e.g., frictional heating, electrical sparking, static electricity) must be present. The resulting fire can radiate more intense heat than an equal amount of gasoline, but it will be shorter-lived than a gasoline fire. Experiments in the U.S., France, and Japan have shown that, once the vapor has been ignited, a flame front burns back through the vapor cloud toward its source (Drake and Reid 1977).

If LNG is released underwater in a tanker accident, it is believed that the vapor will rapidly dissipate due to the heating of the water. The resulting flammable portion of the cloud rising from the water will be much smaller than that from a surface spill of equal size.

There has been much speculation on the likelihood of an LNG spill igniting immediately instead of forming a vapor cloud that drifts some distance from the site of the spill. A 90 percent probability of immediate ignition is assumed in most of the literature reviewed on risk analysis modeling. However, this value is arbitrary, and other values have been used. A vapor cloud explosion intense enough to create a damaging blast wave has not been confirmed, even when a high-exposure charge served as the initiator (Drake and Reid 1977).

Another consequence of an LNG spill is that the superheating of LNG in contact with water can result in low energy, non-chemical explosions. This phenomenon occurred during many Federal government and industry experiments and during the transport of LNG (second voyage of the Pioneer Methane in 1959 when 4,900 gallons of LNG were pumped overboard in a period of 7 minutes, and at a Wisconsin natural gas facility when LNG was drained from storage into a pond). These explosions resulted from sudden vaporization accompanied by a rapid increase in volume. A study conducted by the National Academy of Sciences in 1972 concludes, "The nature of the explosion can be shown to have a relatively low potential for causing physical damage since it is flameless and not supported by the energy of a chemical reaction, only the energy of the superheat" (National Academy of Sciences 1972).

This phenomenon, termed, "flameless vapor explosion," can occur when LNG contacts water and apparently is related to the presence of small amounts of ethane, propane, and nitrogen. No fire or ignition of the vapor occurs, but there is a rapid upward movement of gas accompanied by a loud bang.

After extensive experiments designed to determine the cause of these explosions, Shell Pipeline Research Company concluded that they resulted from a homogeneous nucleation of vapor in a thin layer next to the water surface. The flameless vapor explosion can happen only when concentrations of ethane and propane in the LNG are relatively high.

Delayed vapor explosions can occur as the LNG weathers after a spill. If the initial spill were large, the amount of LNG remaining after weathering could be substantial; however, during the period of weathering, the LNG probably will disperse on the water surface, lowering the probability of a single large explosion.

When a flameless vapor explosion occurs, damage is slight. If such an explosion took place on water adjacent to a tanker, it would have little effect on the hull. Since no chemical reaction is involved, the available energy is limited to the amount of superheat achieved while the LNG is in contact with water (Drake and Reid 1977; Federal Power Commission 1973).

Types of LEG Accidents*

Potential onshore LEG accidents can fall within the following broad categories:

*Unless otherwise noted, taken from U.S. Environmental Protection Agency 1977.

- o Malfunction of Transfer System. The transfer arms, the LEG piping to the storage tanks, and the trestle carrying the piping are sites of possible accidents. The risks associated with these operations have been reduced to low levels by the installation of safety devices. The potential risk to the public has been judged to be small relative to that associated with tanker or land storage tanks.
- o Damage to Storage Tanks. Storage tanks may rupture because of internal causes (e.g., inadequate design, "roll-over" turbulence), or external causes. Roll-over is a phenomenon resulting from improper mixing of LNG from different sources and of different compositions.
- o Malfunction of Vaporization Plant. It is estimated that only small leaks of LNG or gas can occur in the piping from LNG tanks and in the vaporization process. Valve corrosion may occur, leading to leaks and icing, and possible pressure buildups in piping sections. Insulation failures will cause frost, icing, and possible leaks. Safety practices of leak detection, spill prevention and containment, and fire warning devices greatly reduce risks.

When LNG is stored for a period of several months, its constituents (e.g., methane, ethane, propane) evaporate at different rates, resulting in a change in their initial relative proportions, and thus, in an overall change in LNG density. When a new batch of LNG is added to a tank, the old and new LNG volumes may stratify due to density differentials. After a period of time, as convective currents store energy in each layer, the layers can mix or roll over very suddenly, resulting in the boil-off of large amounts of gas. Such a roll-over occurred in 1971 in a storage tank in Italy and it resulted in the venting of 150,000 kilograms of natural gas within 1 hour. Fortunately, the huge amount of vented gas did not ignite and the pressure within the tank did not cause serious damage (Drake and Reid 1977).

Modern facilities utilize standard procedures for preventing roll-over. Stratification is prevented by loading liquids with a greater density into the top of storage tanks. If fresh LNG is always loaded on top, the time required for roll-over is much longer than the typical residence time of LNG in a storage tank. There is general agreement that stratification and subsequent release of excess vapor should not develop spontaneously in an initially well mixed and monitored tank (Chatterjee and Geist 1972; Drake and Reid 1977; Federal Power Commission 1973; Maher and Van Gelder 1972; and Sarsten 1972).

If a spill does occur, damage will be minimized if the tank is diked and located far within the facility boundaries as is required by the strict building codes regulating LNG terminal construction. Dike design is critical to minimizing potential damage. The dike should be capable of containing more than 100 percent of the tank's contents and its location and dimensions selected to assure that damage will not extend beyond a facility's boundaries. The surface area of the dike should be small compared to the volume of any spill. It should also have an insulated floor to minimize heating of the spilled liquid and maintain a low rate of vaporization. Some dikes are broad and shallow, while others extend only a few feet from the edge of the tank, which effectively make them an outer wall. The former promote higher evaporation rates, but are less likely to rupture from the same cause as the tank.

Storage tanks should have double walls to provide good insulation. The inner wall must be of a cryogenic material and an additional safety factor is gained if the outer wall is also cryogenic. In this way, the LNG would be contained to allow draining if a rupture to the inner lining occurred.

Accidents associated with the marine phase of LNG operations may be classified as malfunctions aboard the tanker or impact with another object:

- o On board. On-board malfunctions may involve spills and fires. LNG tanks are designed so that a fire in one tank will not ignite another and care is taken to place tanks as far as possible from potential ignition sources. On-board spills may cause embrittlement and fracture of metal surfaces. Insulated catchments are standard equipment and should contain spills so that the ship and crew are not seriously threatened. Since there are spaces within which LNG vapor may accumulate by accident, the threat of fire cannot be ruled out.
- o Impact with another object. This group of accidents includes collisions, rammings, and groundings. In rammings (ship-to-object impact) and groundings (ship-to-harbor floor impact), the impact point frequently is in the bow. Since the LNG tanks are located aft of the bow, many authorities believe they will not be affected in these types of accidents. A collision (ship-to-ship impact) in which the LNG vessel is struck in its side by another ship is considered to be more serious.

In a collision, only one tank will probably rupture. Rupture of two tanks will occur only if impact takes place at a bulkhead inter-section between two tanks. Consequently, the largest possible amount of LNG to be released will be 75,000 m³ or the contents of two tanks, assuming each contains 37,500 m³.

Several measures may be taken to reduce the possibility of collisions, rammings, and groundings. These include crew training, installation of on-board safety devices, and close Coast Guard surveillance, which would include providing escorts, and excluding other ships in a zone around LNG vessels, or halting all other traffic while an LNG vessel enters and docks.

Past LNG Accidents*

In spite of the potential for severe accidents, there have been only four major incidents involving LNG facilities. The most catastrophic was a 1944 accident in Cleveland, Ohio. A large storage tank containing 38,000 barrels of LNG collapsed, which was later attributed to brittle fracture of the tank wall caused by exposure to cryogenic temperatures. The tank was constructed with an alloy that contained only 2 percent nickel and was not resistant to brittle fractures at temperatures below -76°F. In addition, no dike existed to contain the spill. In the resulting catastrophe, a spreading pool of fire flowed into the surrounding residential and industrial area. Vapor accumulated in closed buildings and sewers and later exploded, demolishing many structures. Fire also spread by thermal radiation from flames near the collapsed tank. Distant combustible materials were ignited and flames reached a height of 2,800 feet. In all, 130 people were killed and 300 injured. Property damage totaled \$10 million, with the destruction of 80 houses and 10 industrial plants. The likelihood of a similar accident occurring has been greatly reduced by the development of materials better able to withstand cryogenic temperatures (alloys now contain 9 percent nickel which can withstand temperatures as low as -328°F), and the containment of spills through diking.

Other accidents have been associated with LNG facilities. In February 1973, Texas Eastern's LNG storage tank on Staten Island exploded and burned. Forty workers were trapped and died in the incident, which occurred during maintenance of the tank lining. Investigators concluded that, although the tank had been emptied of LNG for 1 year, gas vapors had been trapped inside. The flame from a welder's torch ignited them, and the insulation caught fire.

*Taken largely from U.S. Environmental Protection Agency 1977; Office of Technology Assessment 1977.

At a Northwest natural gas facility in Oregon, four workers died when a tank exploded during construction before LNG was introduced. Investigators attributed the accident to careless work practices and not to LNG.

In 1972, natural gas leaked through an air line to the control room of an LNG plant in Montreal, Canada. A large fire followed, creating more damage than would have occurred in an area of less importance.

In 1979, one worker was killed as a result of an explosion at the Cove Point, Maryland, LNG terminal. The cause of this explosion is under investigation.

Recent LNG Accidents

The LNG vessel El Paso Paul Kaiser ran aground near Gibraltar on June 29, 1979. The loaded tanker was stranded because it maneuvered to avoid colliding with a fishing boat. After the ship was refloated and towed to a sheltered anchorage, the 90,000 m³ of LNG was transferred to a sister ship, the El Paso Sonatrach, which delivered the cargo to the Cove Point, Maryland, LNG terminal. The El Paso Paul Kaiser did not release any LNG into the environment even though it received extensive damage. About \$10 million in repairs were expected to be completed in May 1980 (Hale 1980).

On October 6, 1980, an explosion in the motor control center of an electrical substation at the Cove Point terminal resulted from the ignition of natural gas that leaked into the building through an electrical conduit connecting 1 of 10 second-stage LNG pumps. Equipment containing LNG was not damaged and LNG was not released. By the beginning of December, the plant was able to vaporize at its capacity of 500 million ft³ of gas per day (Hale 1980).

Natural Gas Liquids

Natural gas processing plants are assumed to have a lesser effect on air quality than petroleum refineries. This is because the plants are essentially miniature oil refineries with simpler process streams and lower temperatures. Air emissions from natural gas liquids (and sulfur removal plants) emanate mostly from steam generation boilers. In natural gas liquids plants, air emissions total about three tons per 10¹² Btu's processed (based on using 3.1 percent of the gas processed as plant fuel and flaring 0.1 percent). By weight, these emissions are comprised of nitrogen oxides (64 percent), hydrocarbons (21 percent), particulate matter (10 percent), aldehydes (50 percent), and sulfur oxides and carbon monoxide (less than 1 percent). About 1/2 of all air emissions released in gas extraction

processing come from natural gas liquids plants. Most of the remainder--about 45 percent--is attributed to nitrogen oxides emissions from gas engines that drive compressors on gathering pipelines (University of Oklahoma 1975).

No significant amounts of water contaminants are released by natural gas processing plants. Some discharges of lubricants and caustic wastes may occur, but they are treatable by state-of-the-art industrial waste treatment systems. However, the thermal discharge from a natural gas liquids plant is estimated at 25 percent of the energy content of gas used for plant fuel (7.7×10^9 Btu's discharged for each 10^{12} Btu's of natural gas processed). The use of cooling towers can minimize the heat content of the discharge water (University of Oklahoma 1975).

No appreciable solid wastes are associated with natural gas liquids plants. Land use impacts are insignificant, equaling about five acres for a 100-million-ft³-per-day plant.

LEG Facility Security

In a summary of the findings of its Liquefied Energy Gases Safety study, the General Accounting Office (1978) determined that U.S. public utilities and petroleum companies have often been targets of sabotage and that many domestic as well as foreign organizations have the weapons, explosives, knowledge, and capability to sabotage LEG facilities. In urban areas, such sabotage could have catastrophic results, especially if equipment is manipulated to allow the discharge of a spill outside diked areas. The study noted that urban LEG storage facilities are often adjacent to sites that store large quantities of hazardous substances, including volatile liquids. Thus, the ignition of vapor from a spill could lead to the destruction of many LEG storage tanks as well as tanks containing other chemicals at nearby industrial complexes.

Other adverse natural and man-caused incidents have been cited as threats to such industrial installations, including hurricanes, tornadoes, floods, tsunamis, snow and ice storms, earthquakes, land subsidence, avalanches and landslides, volcanoes, meteorites, airplane and missile crashes, and war, as well as worker carelessness (U.S. Environmental Protection Agency 1977).

As the LNG industry continues to expand, especially in the development of peak-shaving plants, and unmanned satellite and storage facilities in urban areas, the public concern focused on safety and security will intensify. Today, the LNG industry is faced with safety and security concerns that are parallel, in the view of a

large segment of the public, to those associated with nuclear power. This concern may spread to include the LPG industry in the future (Tutko 1979).

Responding to the concern, LEG industry officials say that in 30 years of worldwide experience with transoceanic LEG shipping and 18 years with LNG shipping, the industry has had an outstanding safety record. The American Gas Association (1977) points to the following accomplishments:

- o Between 1959 and 1977, 25 LNG tankers completed more than 2,700 voyages without incident.
- o Since it began operating in 1969, the Phillips-Marathon base-load LNG liquefaction facility has operated without incident.
- o The storage of LNG for peak-shaving in the U.S. has expanded from 2 sites in 1965 to well over 100, including satellite storage areas.
- o In a rating of the relative hazards of materials which regularly pass through U.S. ports, LNG has been ranked 19th out of 22 (18 other commodities were considered more hazardous).
- o A variety of risk assessments agree that the risk of fatality from LNG operations is of the same order as, or less than that associated with many common activities such as commercial airline travel, driving, or living in a dwelling.

The facts cited by the trade association reflect the safety of past LNG (as well as LPG) operations. Future predictions based on risk assessment tend to ignore sabotage as a potentially important factor (Van Horn and Wilson 1976). Predictions also ignore threats related to sabotage, which can be acts through stealth, deceit, or in extreme cases, force. The range of such threats are listed and categorized below (Tutko 1979).

<u>Adversary Threat</u>	<u>System Vulnerabilities</u>	<u>Adversary Modes</u>
Terrorists	Sabotage	Deceit
Outside dissidents	Theft	Stealth
Criminal elements	Diversion	Force
Guerrilla activities		
Disgruntled employees		

Environmental Effects

Cooling Water Discharges

A major environmental problem related to the removal of heat by LNG liquefaction facilities is the potential aquatic effect associated with cooling water discharges. The problem is most severe for large liquefaction plants such as one that was proposed (now terminated) by El Paso Gas Company to be located on Gravina Point in Prince William Sound, Alaska. The facility was suggested as part of an alternative proposal for the transportation of Alaskan gas. Planning for the facility was terminated in 1977 when the President and a joint Congressional resolution favored another alternative.

Designs for the proposed plant called for a once-through seawater cooling system with a flow of 658,000 gallons per minute (about 1 billion gallons or 3,000 acre-feet per day). The chlorinated discharge would have had a temperature of 20.7°F above the average ambient temperature of the receiving water of the Sound. Largely as a result of thermal shock, a 100 percent mortality was expected for organisms (e.g., plankton, eggs, larvae, young fish) that entered the system.

For such large liquefaction facilities, cooling towers, or some form of a staged heat reduction process may be required. This would add a substantial cost to construction. Alternatives to the use of a once-through water cooling system include the use of dry cooling towers (mechanical or natural draft), wet cooling towers (mechanical or natural draft), a combination of wet and dry cooling towers, a cooling pond or cooling lake, and a combination of these options. The relative cost ratios for these options as estimated for the proposed El Paso facility are as follows (U.S. Department of the Interior 1977):

<u>Type of System</u>	<u>Comparative*</u>	
	<u>Capital Costs</u>	<u>Operating Costs</u>
Once-through seawater	1.0	1.0
Cooling pond or lake	1.3 - 1.4	1.06 - 1.08
Wet cooling tower		
Mechanical draft	1.3 - 1.4	1.08 - 1.11
Natural draft	1.8 - 2.0	1.14 - 1.22
Dry cooling tower		
Mechanical draft	3.2 - 3.4	1.68 - 1.88
Natural draft	6.4 - 7.0	1.98 - 2.42

A significant environmental issue related to the use of cooling water within an LNG liquefaction facility is the entrainment (organisms drawn involuntarily into the plant with the cooling water) of all pelagic/planktonic organisms and other smaller organisms not capable of avoiding or swimming against the intake current. For large facilities, entrainment may result in the deaths of 100 percent of all living organisms entering the plant.

Three factors leading to the 100 percent mortality rate for all entrained organisms are:

- (1) A high and rapid heat gain above ambient temperature;
- (2) Contact with a chemical biocide; and
- (3) Pressure changes and turbulence induced by pumping.

A 100 percent mortality rate, coupled with the tremendous volumes of water used, can result in heavy losses of phytoplankton and zooplankton, along with the egg, larvae, and juvenile stages of larger organisms in the surface water used as a water supply, especially if a large portion of the body of water passes through the plant within a short period of time.

*As a point of reference, capital costs for a large natural draft wet cooling tower for a large utility plant in the contiguous 48 states amounted to about \$90 million in 1976 (Power Engineering 1976).

There are also several environmental problems related to the once-through cooling system outside of the LNG facility. These include (Brown and Helfand 1977; Kalberer 1980):

- (1) Impingement of larvae and juvenile organisms on traveling screens at intake. This is a serious problem at power plants and a potentially serious problem at large water cooled liquefaction plants, especially during the spring and summer months.
- (2) Chlorine. An unknown, but large amount (owing to the huge volume of water treated) of the free chlorine used as a biocide within the cooling system will be released into surface waters. Chlorine in a free or complexed form is extremely toxic in low concentrations.
- (3) Heated effluent. The adverse environmental effects of heated water include the following:
 - (a) Thermal shock (both standard high temperature shock and the shock that can be experienced by organisms accustomed to a high temperature when a plant is shut down and the temperature drops).
 - (b) Behavioral changes (e.g., changes in migration routes, thermal barrier, feeding behavior).
 - (c) Physiological changes (changes in the temperature-specific life history stages of organisms, i.e., premature spawning or delayed migration, accelerated development of larval and juvenile stages).
 - (d) Increased metabolic rate (which leads to increased susceptibility to pathogens and pollutants).
 - (e) Increase in pathogens. (High temperatures increase diseases of low temperature organisms.)
 - (f) Supersaturation of atmospheric gases (leads to lethal gas bubble diseases in fish).
 - (g) Establishment of exotic species.
- (4) Heavy metals. These may be toxic to marine organisms through their action in the cooling system discharge stream. The heavy metals that can be present in the seawater cooling system discharge stream of a liquefaction plant include aluminum, copper, and zinc (these also may be a problem in

some freshwater systems). The sources of these metals are the seawater exchangers which utilize aluminum brass for exchange tubes. Given an erosion-corrosion rate of two to five mils per year and the surface area that is exposed to metal loss, the heavy metal concentration in the discharge stream contributed by a large LNG plant can be 31 to 77 parts per billion (ppb) by weight. Of the three metals, only copper is highly toxic to marine life, and an LNG plant's contribution to the total concentration can be in the range of 24 to 59 ppb. For comparison, the concentrations of the three metals normally found in seawater are: aluminum, 10ppb; zinc, 10 ppb; and copper, 3 ppb.

Other impacts on aquatic resources include brine emissions from desalination facilities (various forms of marine organisms may be affected by variations in salinity); water pollution caused by tanker operation and other wastes associated with facilities supporting the LNG plant; removal of fish habitat through the construction of pier facilities; and some interference with and disruption of commercial fishing operations and sites.

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SUMMARY OF RESEARCH NEEDS

Research needs related to liquefied energy gases fall into two major areas: those concerning health and the environment. These areas are discussed below.

Health

Risk Assessment

A recent, major energy assessment (Strobaugh and Yergin 1979) said:

"Some scientific experts have claimed that the handling and transportation of LNG poses great hazards to the public. Accidents to LNG tankers entering port or while unloading, accidents at LNG storage facilities, and motor vehicle accidents involving trucks that transport LNG--all threaten the public with the risk of potentially catastrophic explosions and fires. Equally reputable scientists support the gas industry's view that such risks are under control. They cite the special design features and operating requirements of LNG ships and storage facilities as protection against catastrophe, and argue that highway transport of LNG is no more hazardous than the transportation of gasoline.

"As with the nuclear safety controversy, there seem to be serious gaps in government-sponsored research and development programs to answer the issues that are in dispute. There is, for example, no good experimental basis for predicting the consequences of a collision between an LNG ship and another vessel. Gaps in scientific knowledge such as these create so much uncertainty that a wide range of risk assessments is possible."

This statement would indicate that a well structured and rigorous risk assessment is needed. It could deal comprehensively with current and projected LNG imports, domestic production, LNG transportation and movement patterns, and with the probability of sabotage.

Natural Gas Liquids

Since no appreciable solid waste or liquid emissions occur from natural gas liquids plants, no technology-specific aquatic or terrestrial effects research appears warranted. Air quality may be affected by emissions of nitrogen oxides, hydrocarbons, particulate matter, and aldehydes. Much research has focused on the effects of nitrogen oxides and particulate matter on air quality. Thus:

- o No new NGL technology-specific research appears to be warranted with respect to nitrogen oxide.
- o The nature, reactivity, and metals content of the particulate matter emitted from natural gas liquids plants may need to be determined.
- o The toxic properties as well as the constituents of the hydrocarbon component of the emissions from natural gas liquids plants may need to be examined with state-of-the-art methods and equipment. The nature and air quality effects of aldehydes associated with natural gas liquids plants may need to be examined, especially with respect to their interaction with other air quality parameters.

Environment

Cooling Water Discharges

Research may find beneficial uses for waste heat. The large quantity of water required by a liquefaction facility for cooling provides a significant potential for energy recovery. Research is needed to explore this option for future U.S. liquefaction plants. Information already developed in this area for coal and nuclear power plant effluent waters should be applied to liquefaction plants. Feasibility studies should focus on using waste heat for wastewater treatment (e.g., enhancement of flocculation, desalination, drying of sludges, evaporation of wastewater), for residential and commercial heating, and for freshwater aquaculture or mariculture. (For potential options see University of Maine 1979; Hari et al. 1974.)

The cold temperatures associated with regasification may provide a benefit through energy conservation and cost reduction. The cold waters can be used to cool heated power plant and industrial effluent waters, thereby eliminating thermal impacts from both sources.

Baseline Aquatic Studies

Baseline aquatic studies should be performed to gather information on the assimilative capacity of the aquatic environment potentially impacted by discharges from future liquefaction plants. Such studies should include collecting information related to flushing and turnover rates of the receiving water, the effects of water temperature on the timing of invertebrate and fish spawning and on the rate of development of aquatic organisms, and the composition and diversity of plant and animal aquatic populations with respect to temperature tolerances (species that are tolerant of warm temperatures will thrive and cold water species will be eliminated).

Use of Air as a Heat Sink

Basically, liquefaction is achieved by using a refrigerant to remove heat from a gas at a low temperature and to transfer it to another medium, i.e., cooling water. The heat also can be transferred to atmospheric air. The feasibility of using air as a medium for waste heat disposal in large liquefaction facilities should be explored and the potential resultant atmospheric effects should be assessed.

Part 6

Transportation and Storage

TRANSPORTATION AND STORAGE SUMMARY

This section identifies several research needs associated with land transportation. A health risk assessment is needed, for example, to define the level of exposure of pipeline construction workers to coal tar pipe coatings, coal tar saturated wrapping materials, and asphalt coatings and wrapping materials. The toxic properties of ethanolamine should be studied more closely, especially with respect to dermal exposure. The potential for nitrosamine formation should be examined when ethanolamine is exposed to ambient air. Safety procedures need to be developed to protect the public from unguarded deep trenches during pipeline construction through urban areas.

Research needs related to marine transportation are also identified here. A port health and safety study should be initiated which would address best case conditions with respect to pumping, inerting, venting, and purging to minimize impact upon air quality. Such a study should include guidelines for assumptions used to evaluate emission rates associated with proposed new marine terminals.

Finally, this section notes that environmental research should focus on the following areas: plant mycorrhizal associations as they are affected by crude and products; degradation of petroleum by soil biota under differing soil conditions (especially those of the semi-arid West and the Appalachian Basin subject to new oil and gas development); effect of spilled crude and products on soil bacteria, fungi, and other biota and their capacity to recover to normal levels; and the effect of vapor phase and gaseous hydrocarbon organics (including natural gas) on soil biota as a result of underground pipe ruptures.

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OIL AND GAS TRANSPORTATION AND STORAGE

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OIL AND GAS TRANSPORTATION AND STORAGE

TECHNOLOGY DESCRIPTION

Crude oil, petroleum products, and natural gas are transported on land and fresh water* to refineries, storage areas, and markets, utilizing tank trucks, railroad tank cars, barges, and pipelines. The choice of the mode of transportation depends on the distance traveled, the nature of the material being transported, the availability of the transport system, and other factors.

History of Oil Transportation

In the early 1800s, oil was collected from surface deposits and sold as medicine and for lubrication or lighting. Following the "Drake" oil well completion in 1859, crude was carried in wooden barrels to western Pennsylvania refineries by riverboats, horse-drawn wagons, and railroad flatcars. Charging only 1/20th of the price for the same service, pipelines quickly replaced other forms of oil transportation by 1900 (Brown and Helfand 1977a).

After 1900, crude production shifted from the east-central states of Pennsylvania, Ohio, Indiana, West Virginia, and Kentucky to newly discovered fields in Texas, Oklahoma, Louisiana, and California (Figure 1). By 1940 more than 85 percent of crude supplies to eastern refineries were derived from production areas west of the Mississippi River (Brown and Helfand 1977b).

To aid acceleration of oil pipeline construction during World War II, Congress passed the Cole Act in 1942 which allowed the President to grant a petroleum pipeline company the right of eminent domain when acquiring land and rights-of-way during wartime. Within 2 years accelerated construction provided a total of more than 11,000 miles of new pipeline, 3,000 miles of relocation and modernization of older lines, and 3,000 miles of reversed flow in existent lines. Pipeline flow increased from pre-war levels of less than 50,000 barrels a day to 754,000 (Brown and Helfand 1977b). In 1980 over 11,000 miles of oil and gas liquid pipelines were under construction in the U.S. and Canada (Hale 1980).

*See the Offshore Development section of this report for information related to marine transportation of oil. Marine transport of gas is addressed in the Liquefied Energy Gases section.

Source: Brown and Helfand 1977a.

FIGURE 1
GROWTH OF CRUDE OIL PIPELINES IN THE UNITED STATES

After the war many oil pipelines were taken out of service, reversed, or converted to gas pipelines as military demands declined. Tankers soon became available for inter-coastal shipments. During the war, large diameter trunk lines (20 to 24 inches) proved capable of transporting considerable amounts of oil at a lower cost than the pre-war small diameter lines (less than 16 inches). This marked the beginning of a new era in U.S. pipeline construction, characterized by the building of large, long-distance pipelines. The trend began in the 1950s and continues today. Many of the older lines have been removed, used for the transport of products (gasoline, kerosene, turbine fuel, diesel fuel, and heating oil), or converted for the transmission of natural gas.

In the early 1900s, many oil seeps were discovered in Alaska, but further exploration determined that these were not economically recoverable. However, discoveries of oil along the south-central Alaskan coast in the 1950s and 1960s led to a modest production peak in 1970 of about 80 million barrels. Following the North Slope discovery in 1958, oil consultants have estimated that the new field contains 5 to 20 billion barrels, or even as much as 50 billion barrels (Figure 2).

After a series of court injunctions and trials, the Trans-Alaska Pipeline Act of 1973 authorized construction of the Alaskan oil pipeline. Work began in 1974 under the direction of Alyeska Pipeline Service Company and involved the construction of almost 800 miles of 48-inch pipe, twelve pump stations, three crude topping plants (which provide turbine fuel for pump stations), an oil storage and shipping complex at the southern terminus in Valdez, and other support facilities. Completed in 1978, the pipeline has a normal flow of 1.2 million barrels a day.

At present, proven economically recoverable reserves in the Prudhoe Bay field amount to about 9.6 billion barrels (Figure 2). Other North Slope reserves and those under the Beaufort Sea are expected to bring the total proven reserves in North Alaska to 15.1 billion barrels by 1989. As these reserves are brought on line, production should peak in 1985 at about 3 million barrels a day, which would equal 21 percent of total U.S. crude production. Maintaining the flow after this time will depend upon new finds in existing fields or in new fields such as the National Petroleum Reserve in northwest Alaska. New pipelines (both oil and gas) will be needed to tap these sources.

History of Gas Transportation

Early records refer to gas being piped through bamboo in 10th century China, to wells drilled for natural gas in 7th century Japan,

Note: NPRA = Naval Petroleum Reserve in Alaska.

FIGURE 2
ALASKA PRODUCTION AREAS

and to the famed Greek oracle at Delphi, where men breathed gas and became lightheaded. In 1577 the Belgian chemist Van Helmont observed a "wild spirit or breath" burst forth from a material being heated in his crucible. He named the substance "gas" after its similarity to a "geist" (a German word for ghost or spirit). Manufactured gas, produced in 18th century Europe by heating coal in the absence of air, soon replaced the candle and oil lamp as a principal source of illumination. Gas manufactured from coal or oil is still being burned in many countries, but has largely been replaced by less expensive and more convenient natural gas.

Gas companies were established in 1812 in Europe and in 1816 in the U.S. By 1859 more than 300 U.S. cities were illuminated with gas. Today natural gas meets over 20 percent of the world's energy requirements and about 30 percent of U.S. energy needs. It supplies more than 50 percent of the gross energy input to household, commercial, and industrial facilities in the U.S. In addition to its use as a fuel to produce heat and light, natural gas is used as a raw material in the production of chemicals including antifreeze, fertilizers, pesticides, solvents, and synthetic fibers.

As reserves were discovered, long distance pipelines were constructed. Early U.S. pipelines consisted of bored logs joined together and tarred to form wooden pipes which lasted up to 75 years. The first major iron pipeline served the city of Titusville, Pennsylvania, in 1872. Steel pipes and electric welding came on line in 1887 and 1931, respectively. In 1947, a major change in the gas industry occurred when natural gas from the Southwest was transported to the East Coast through large crude oil pipelines abandoned after World War II (Brown 1978).

Since 1950, the gas utility industry has experienced significant growth, expanding from 400,000 miles to approximately 1 million miles of gas pipelines. The industry also has experienced recent growth in the storage and marine transport of liquefied natural gas (LNG). When refrigerated to -258°F (-161°C), natural gas can be condensed from 600 cubic feet of gas to 1 cubic foot of liquid, which greatly reduces the volumetric capacity needed for storage or containerized transport. Past use of LNG has largely been dedicated to reserves for peak load service. Recent development of an LNG tanker industry has provided supplemental natural gas for baseload service supplied by gas pipelines. Since 1971 natural gas imports, primarily by pipeline from Canada and Mexico, have accounted for about 5 percent of the annual domestic consumption of natural gas. In 1978 only about 1 percent of these imports were in the form of LNG.

An ongoing project to move Alaskan gas across Canada to markets in the contiguous states will result in the largest privately

financed energy project in history--a 4,782-mile system at a cost of \$11 to \$14 billion. This project, which has received final Federal approval, was selected after exhaustive debates before Federal and state agencies and Congressional committees, as well as numerous assessments of environmental, social, and economic impacts. Federal regulation of this pipeline is to be provided through a Federal inspector (a new concept in regulation) who will provide a "one-window" approach intended to simplify the regulatory process, reduce costs and delays, and avoid unnecessary duplication of efforts in builder interactions with various Federal agencies (Brown 1978).

Generic Description of Oil and Gas Transportation

Oil Transportation

Tank trucks, railroad tank cars (tankers are covered in the Offshore Development section of this report), and pipelines are used for domestic transportation. Tank trucks carry relatively small quantities for distances of less than 500 miles. Railroad tank cars generally are most cost effective for distances greater than several hundred miles and for tank car quantities. Utilized in coastal waters, tankers carry Alaskan crude to coastal ports. Barges are utilized in major inland waterways, usually in the transport of petroleum products. Both tankers and barges are used for long-distance and large volume transportation, but are limited by available port facilities.

Oil pipelines are competitive with waterborne and railroad transportation. Pipelines are constructed of welded steel and are as large as four feet in diameter. Pumping stations, which utilize centrifugal pumps and reciprocating engines powered by electric or diesel engines, are located every 50 to 100 kilometers to compensate for pressure drops. The primary efficiency of the various oil transportation methods is nearly 100 percent. Land losses are limited to leaks or spills. Although a threat to the environment, these spills constitute much less than 1 percent of the total amount of oil transported, as indicated in Table 1. That table also shows ancillary energy requirements for different transport methods. These are not comparable because each method is depicted by data for oil transported over different distances.

Gas Transportation

Most domestic gas is transported by buried steel pipelines with diameters also as large as four feet. The gas usually is compressed to 600 to 1,000 pounds of pressure per square inch and this pressure drives the gas through the pipe. Valves installed every 10 to 30 miles allow for isolation of a pipeline section if a large pressure

TABLE 1

VARIOUS ESTIMATES OF OIL TRANSPORTATION EFFICIENCIES

Method	Primary Efficiency (percent)	Ancillary Energy (10^9 per 10^{12} Btu's)	Overall Efficiency (percent)	Distance for Ancillary Energy (miles)
Pipeline ^a	100.0	3.69	99.3	300
Pipeline ^b	U	U	99.1	NA
Pipeline ^c	99.6	U	U	NA
Tankers and supertankers ^a	99.6	40.7	95.8	10,000
Tankers and supertankers ^b	U	U	99.5	NA
Barges ^a	100.0	25.7	97.4	1,500
Barges ^b	U	U	99.6	NA
Tank trucks ^a	U	14.1	U	500
Tank cars ^a	U	14.6	U	500

Notes: U = Efficiency unknown.

NA = Data not available.

a, b, and c = Different estimators.

Estimates are subject to a possible error of 25 percent or less.

Source: University of Oklahoma 1975.

drop occurs. Gas pipelines are coated to protect them from physical (abrasive), chemical, and electrolytic activity. In urban areas, corrosion as a result of electrical currents may be enhanced. Stray electrical charges may cause loss of metallic ions, resulting in a weakening of the pipeline. One mechanism to offset this problem is the use of cathodic protection in which a direct current is applied to the pipe.

Pipeline Construction

Preliminary Steps. The construction of a typical pipeline begins with preparatory procedures that may involve construction of roads, storage facilities, pumping stations, control and ancillary facilities, and temporary housing. Rights-of-way widths must be surveyed and staked.

Next the land must be cleared and graded. Clearing involves the removal of trees, brush, crops, boulders, and buildings in the ditch line that would interfere with ditching machine operations. Grading requires leveling the ground surface as necessary for vehicles and equipment so the pipeline may be placed at the desired elevation. Construction of bridges, diverting streams, embankments and storm-water diversion trenches, and the stabilization of soil to support heavy equipment is required.

During this activity, fences may need to be crossed. This requires the construction of temporary gates, usually of wire. Gatekeepers may be needed to keep livestock from straying or to prevent improper use of the passageways. Following construction, these fence openings need to be repaired.

Pipe Storage and Handling. Sometimes the line pipe is strung before the ditch is dug and sometimes afterward, depending on local conditions and contractor preference. This often leads to safety hazards because, in many instances, the ditching activities and the pipeline supply operation are handled by separate contractors who operate on different time schedules driven by variations in economic incentives, efficiency of operation, and convenience. Often the deep trench is left open and unguarded for several months before the pipeline is delivered.

The line pipe and casing pipe is hauled over public roads, which requires licenses and permits from Federal, state, and local agencies. With double-jointed pipe, special routes must be carefully selected to avoid sharp turns and weak bridges. Should storage be required before the string is laid, care must be taken to keep the pipe from sinking into the ground, to distribute pipe weight to prevent flattening or other deformation, and to prevent or control

corrosion, especially at the beveled edges of the pipe (Petroleum Extension Service 1973).

Coating materials, gate valves, fittings, and pipe must be hauled to the right-of-way and strung (i.e., distributed in the places where they will be needed for construction). The pipe is usually loaded onto trucks and unloaded by tractors or trucks fitted with sidebooms. Care must be taken to avoid damaging pipes and coatings.

Ditching. Ditching includes all excavation work required to provide a ditch of the specified dimensions and depth of pipe cover. Depending on topography and location, the depth of the ditch may vary from a few feet to dozens of feet. The trenches usually are dug to provide at least a foot clearance on each side of the pipe. Trenching is by mechanical, wheel-mounted, self-propelled, or tractor-drawn ditching machines; single-toothed rippers; or sometimes by backhoes. Explosives may be used where rock or permafrost is encountered. Burial is the preferred method of crossing stream beds, except where high scouring rates exist.

Pipe Bending. The pipeline must conform to the terrain and contour of the ditch, both vertically and horizontally. The pipe is bent using heavy, hydraulically operated machines mounted on tracks or skids.

Welding. Welding in the field is performed both manually and with automatic equipment. The welds are subjected to inspection with visual, mechanical, electronic, and x-ray techniques to ensure integrity.

Coating and Wrapping. This procedure is for pipe protection. The wrapping material is chosen for its resistance to soil corrosiveness and chemical content of the groundwater. Coating and wrapping materials include asphalt, asphalt-saturated paper, somastic (asphalt and sand), coal tar with coal tar-saturated paper, butyl tape, or thin film epoxy. Concrete coatings and collars are also used, especially for stability when pipes cross waterways and wetlands.

Pipe Laying. The lowering-in operation normally is integrated with the welding, bending, coating, and wrapping sequence in major pipeline projects and requires specially designed equipment. Commonly, sideboom, crawling tractors are used to lower the pipe into the trench. Swabbing is performed to reduce the amount of foreign matter remaining after welding.

Backfilling and Cleanup. After the pipe is placed, the excavated material is backfilled. It may be necessary to pad the pipe

with processed soil or sand. Special techniques are required to prevent frost heave, maintain aquifer movement and surface and tile drainage, and to prevent crushing under highway and railroad traffic corridors. Site cleanup, revegetation, and restoration are required. This involves disposing of unused excavated materials, construction wastes and debris, and the removal and obliteration of temporary camps, roads, and storage areas. If pipeline work is conducted in winter, revegetation and restoration will carry over into summer. More than 1 year may be required to restore the land (or to retain its natural surface configuration with proper backfilling) and reestablish the vegetative cover.

Pipeline Testing

After construction and before operation, a pipeline is tested hydrostatically (usually with air) for leaks in the pipe or welds, and to verify structural integrity at expected operating pressure. In cold areas such as Alaska, a methanol solution or air may be used to test gas pipelines (see U.S. Department of the Interior 1977 for a discussion of the pros and cons associated with each testing method). With hydrostatic testing, care must be taken to avoid discharging contaminated water into natural draining courses. Usually, test water, which accumulates metals and products of corrosion and welding, is stored and used again without discharge. When construction progress is in the direction of oil flow, oil can be used to displace water from successive sections of the pipeline as construction is completed.

Pipeline Maintenance

Usually compressor stations are designed to operate automatically by remote control. Mainline block valves, located at about 20-kilometer intervals, serve to close portions of the pipeline for repair. Pipeline scrapers or pigs are used for internal cleaning and are released and captured in specially designed traps. Right-of-way inspections are a continuous activity involving aerial surveillance, mechanized patrol, or sometimes foot patrol. Usually this activity also includes the maintenance of a right-of-way permanently cleared to a width of 50 feet.

Pipeline Gas Processing

Separation, Compression, Drying. Fluids from both oil and gas wells are usually first processed through a free water knock-out separator to remove water and sand. They then pass through a separation sequence. Both water and water vapor must be removed from natural gas to prevent the formation of methane hydrates (solid snow-like compounds of water and methane). The hydrates are formed when

the gas cools as it expands. Hydrates can plug wellhead valves, metering equipment, and pipelines. If hydrate formation is a problem at the wellhead, the produced fluids can be heated prior to flowing into any gas processing equipment.

After water and sand have been removed, the hydrocarbons are passed through a low-pressure separator and split into oil and gas streams. The separation of associated gas (gas occurring with the oil either free or in solution) and condensates may be performed in several stages to increase the recovery of liquid hydrocarbons (Figure 3). The gas also may be dried using a glycol process in which a combination of heat and a glycol vapor are used to dry the gas (University of Oklahoma 1975, 1979).

The type of gas produced and the extent of separation needed determines, in large part, the amount of gas marketed from a particular hydrocarbon reservoir. Normally, a fluid stream rich in natural gas is processed using a single-stage, low-pressure separator. However, the gas recovered from a single oil-gas separator frequently cannot be economically compressed and transmitted to shore or to an existing gas transmission line. Such gas, in past years, was vented to the atmosphere or flared. It may be returned to the reservoir in order to enhance the recovery of liquids from gas condensate reservoirs or crude oil from crude oil reservoirs containing gas caps.

As pressures are normally high in the early production life of a gas reservoir, compression may not be needed to transmit the gas through the gathering system until the later years of the tapped reservoir's life. In an oil-gas reservoir, however, compression is needed throughout the life of the reservoir because all fluids are passed through low-pressure separators. Depending on the type and stage of the reservoir, no compression may be needed, a single wellhead compressor may be used, or an extensive central compressor complex may be required (University of Oklahoma 1975).

Desulfurization. The process of removing sulfur from natural gas is adjunct to other natural gas processing steps (e.g., field separation, natural gas liquids removal, compression) and in many situations may be used in conjunction with them. The process involves removing hydrogen sulfide (H_2S) from natural gas in which its relative concentration may range from 0 to 76 percent. As with crude oil, natural gases containing relatively high concentrations of hydrogen sulfide are termed "sour;" whereas, those that are essentially free of hydrogen sulfide are termed "sweet."

Sour gases present several problems in the processing and handling of natural gas. They are extremely toxic and corrosive. When burned, they may produce substantial amounts of sulfur dioxide

FIGURE 3
TYPICAL NATURAL GAS PROCESSING SEQUENCE

(SO₂) or sulfur trioxide (SO₃). Thus, when sour gas is extracted and processed, special grades of steel must be used in the construction of wells, well equipment, gathering field pipelines, and treatment facilities.

Because of its toxic and corrosive properties, H₂S is removed in desulfurization plants before the gas is transported by pipeline and marketed. The process which is most commonly used involves the extraction of hydrogen sulfide through the use of a solution of ethanolamine. This process removes carbon dioxide and almost all of the hydrogen sulfide (Figure 3). After removal from the gas and regeneration of the ethanolamine solution, the hydrogen sulfide often has been flared in past years, resulting in a discharge of sulfur dioxide directly into the atmosphere. Today, up to 95 percent of the hydrogen sulfide is converted to elemental sulfur. New--but expensive--techniques allow for the recovery of 99.9 percent of the sulfur in sour natural gas (University of Oklahoma 1975).

Pipeline Regulation

Both the gas and oil pipeline industries are heavily regulated with respect to health, safety, and the environment. Regulations relate to pressure testing, weld integrity, safety, and air emissions. Regulating agencies include the Federal Energy Regulatory Commission, the National Transportation Safety Board, the Department of Transportation (DOT), and the U.S. Environmental Protection Agency. Pending legislation (PL 196-29) is designed to give DOT the authority to promulgate safety regulations for liquid as well as gas pipelines.

DOT issued amendments to CFR 49 Part 195 that, for the most part, became effective July 15, 1980. These rules include highly volatile liquids (HVL) for the first time and impose more stringent requirements. For example, pipeline operating manuals must contain more detailed information than was formerly required. The monitoring of pressure, temperature, and flow from unattended stations is required unless the facility is equipped with fail-safe devices; and, the requirements for training and public education are more extensive.

The Environmental Protection Agency is also stepping up its activities. For example, it is becoming increasingly difficult to obtain permits to construct and operate new storage tanks. Tanks handling liquid petroleum products between approximately 1.5 and 11.5 psia vapor pressure must submit to Prevention of Significant Deterioration (PSD) review, which may require site monitoring and offset activities. As a result, liquid pipeline projects may easily be delayed for several years while permit requirements are being resolved (Polasek 1980).

Alternatives to Normal Transportation

Over the years several exotic ideas have been proposed for the transportation of oil and gas. Some may be utilized in the future, and they include:

- o Submarine Tankers. The General Dynamics Corporation of New York has proposed a 900-foot-long submarine tanker that can carry a 170,000-ton cargo. Oil or LNG would be carried almost everywhere in the sub, except for a portion in the center pressure cylinder reserved for living and machinery space.

The sub-tanker could travel long distances, even under polar ice, and could easily travel through tropical storms. The tanker could be fully loaded from undersea terminals or off-shore platforms and surface to discharge at coastal or inland ports.

Also proposed is that the submarine or a tug boat pull submerged oil tank trains, cement barges, or large rubber containers of crude oil. These units could be transported inland by rivers and canals.

- o Hovercraft. Another proposal involves using hovercraft (surface effect ships and vehicles, air cushion vehicles, and captured air-bubble ships). These heavy transport vehicles could provide an ideal air-water-land interface for coastal wetland or rugged terrain transport of relatively small volumes of oil to remote areas. The method offers flexibility of destination at a speed faster than ships and slower than aircraft. It also provides the shipping economy of large tankers and rail tank trains, and the possibility of year-round transport (Dyas 1972).
- o Aerotankers. An unusual proposal is to employ airplanes or cargo planes. The Boeing aircraft company has developed plans for a mammoth plane with a wingspan of 478 feet (compared to 195 feet for the 747), requiring the thrust of a dozen jet engines to lift its 3.5 million pounds gross net weight. This "resource carrier" could carry 8,100 barrels of oil or LNG in two wing-mounted detachable cargo pods.
- o Ice Breakers. Ice-breaking tankers have been proposed for both LNG and crude oil. There is at least one known design for an ice-breaking supertanker to carry oil from the arctic area, but none has actually been built. The largest ice-breaking vessel which has operated in the arctic thus far is

the 114,668-dead-weight-ton MANHATTAN, which made two voyages in 1969 and 1970. Those voyages should provide sufficient data to permit the design of a hull configuration that would withstand the forces and accelerations of ice breaking. The characteristics of an adequate hull configuration would be an ice-breaking bow of the standard type (experiments with "novel" ice-breaking bows have given poor results), addition of a high-tensile steel ice-belt to protect areas of shell plating exposed to ice damage, and additional hull framing and stiffening members (Dyas 1972; U.S. Department of the Interior 1976).

- o Dirigibles. Interest in dirigibles for cargo transportation has been rising since the first international conference on dirigibles was held in 1973. Thus, the possibility of using this method for LNG transport warrants mention.

Sonstegaard has studied the possible transport of LNG by dirigible on the principle that the cheapest way to transport a commercial gas could be to put it in a streamlined bag and float it in the atmosphere. According to his findings, reported in 1970, natural gas could be transported by large dirigible airships from as far as the Alaskan North Slope to the New York-Philadelphia area at a price (based on 1970 figures) competitive with gas pipelined from the Gulf Coast region.

Most persons at the international conference on airships believed a possible use date was at least 10 years away. Shell Oil Company has experimented with the use of smaller blimps to transport natural gas from the Middle East in lieu of building foreign LNG plants (U.S. Department of the Interior 1976).

Natural Gas Storage

Natural gas storage and transfer technologies are old and well established. Facilities were established to meet a demand that varies over a 24-hour period and is seasonal. Thus, storage facilities primarily function to equalize pressures and meet peak supply demands placed on pipelines and gas delivery systems. Pipelines are generally designed for a delivery rate roughly equal to the average demand rate. Excess gas delivered during periods of low demand is stored for use during peak demand periods. Operation of pipelines near their capacity with high loads minimizes unit transportation costs.

The first recorded experiment in storing gas underground was successfully accomplished in Welland County, Ontario, in 1915. Several old wells were reconditioned. Then gas was injected into the partially depleted field, and withdrawn the following winter to meet peak requirements. The next year, the first storage operation in the U.S. was begun in the depleted Zoar Field near Buffalo, New York. This storage reservoir is still in operation. Subsequently, techniques were developed to store gas in depleted water sands (aquifers), salt caverns, coal mines, and tanks. In 1978, over 68 billion cubic feet of gas was in storage, of which 54 billion cubic feet was in underground storage.

Underground Gas Storage

Normally, natural gas is stored underground in depleted gas reservoirs, but depleted oil reservoirs are also used. Water-bearing formations or aquifers, dug caverns, and sealed mines have been used in areas where depleted gas or oil fields are unavailable.

In most underground, depleted gas or oil field reservoirs, water present in porous media is the confining mechanism; the stored gas tends to form a bubble (Katz 1980). Caprocks normally are low permeability rocks filled with water. The pores are so small that gas pressure cannot displace the water at prevailing pressure differentials due to surface effects. Underneath the gas-saturated reservoir, water-filled zones prevent the gas from moving downward or laterally. It is taken for granted that the caprock can withstand pressure from the buoyed gas reservoir, for the same caprock previously held a gas or oil deposit through a substantial geological time span. However, extensive testing is conducted and structural safety factors are built in. Leakage may occur due to such anomalies as caprock fractures, faults, solution cavities, "pinching-out" around the caprock, and leaks around well casings.

It is reportedly common to hear the hissing sound of gas leaking at storage fields (Katz 1980). Gases are stored under pressure, from several hundred to several thousand pounds per square inch, and fugitive leaks from valves, flanges, compressors, well heads, and joints are inevitable. Gas in the atmosphere of audibly leaking equipment at one location has been measured at 5 to 10 ppm--well within the safe range for occupational exposures. Like the distribution of leak sources within a refinery, a few sources account for a large proportion of the loss. The orifice tap and other equipment under the highest pressure are likely to emit detectable leakage. Losses from such leakage, if unrepaired, may run into millions of cubic feet per year (a small percentage of the gas stored).

Techniques developed to measure gas losses have shown that an audible leak could cause the loss of 1 billion cubic feet per year. Within well bores, temperature and noise logs are used to detect leakage areas where gas expansion creates a temperature drop and detectable pressure waves. Storage operators closely monitor their reservoirs and underground gas movements, and repair leaking equipment.

Gas storage reservoirs normally have operational lifetimes of 30 to 50 years or more. Over this period, some gas can leak through casings or caprock to enter zones above the intended storage zone. The gases may eventually reach local water supplies, permeate surface soil, and enter buildings or their water supplies, creating explosive mixtures. This rarely occurs and storage operators may place monitors on water supplies and in basements in the immediate area.

Pressures in oil or gas reservoirs are described in pounds per square inch per foot of depth. Internal pressures alone would fracture reservoir caprock and cement structures if it were not for the counterbalancing, depth-dependent external pressures which relieve much of the strain.

Prior to storage and transmission, natural gas is cleaned of hydrogen sulfide, carbon dioxide, water, and other contaminants. When gas is transferred up from underground storage, it may contain some H_2S due to contamination from caprock or oil within the reservoir. Exiting gases may be periodically or continuously monitored for H_2S concentrations. Natural gases may naturally contain traces of oxygen and occasionally compressed air is added to dilute overly rich (high in ethane and propane) gases to normal heating values. Propane-air mixtures may be stored or transported for injection into the storage or distribution stream as a method of meeting peak demands.

Aboveground Gas Storage

Aboveground tanks or gasholders are used to meet daily peak demands in local distribution systems. The use of these tanks is declining since they are being replaced by liquified gases peak-shaving plants. Gasholders are frequently of the lifter-roof type that is also used for petroleum products storage.

The Gas Storage Industry

As of November 1978, there were 396 underground storage fields belonging to 91 companies, of which 10 fields were under development. Nearly all storage facilities are operated for natural gas pipeline and regional consumption peak-shaving operations. For 1978 to 1979,

the gas industry had the potential of feeding 80 to 84 billion cubic feet or more total peak day sendouts into distribution (pipeline) systems. Underground gas storage provides most of the nation's storage capacity (over 54 billion cubic feet). Reservoirs may hold varying proportions of injected and native gas, i.e., gas remaining in the reservoir from its previous use as a gas or oil well (Hale 1980).

Gas storage facilities are primarily located near major gas consumption areas and natural gas fields. Most facilities are clustered in the northern Appalachian and Indiana-Illinois-Kentucky regions.

Gas Storage Emissions

Negligible air pollution results from underground and above-ground gas storage. However, products of combustion are emitted by compressors required for injection and withdrawal. Methane, the major constituent of stored natural gas, is not photochemically active and does not result in ozone production.

A leaking reservoir may permit gases to enter local aquifers, but this is usually remedied quickly; the gas dissipates rapidly and constitutes little toxic hazard, although occasionally it may pose a safety hazard by creating an explosive mixture that accumulates in an aboveground confined space. Natural gas that leaks to the surface may also accumulate in depressions, disrupting sensitive vegetation.

Natural gas storage poses few occupational health hazards under normal operating conditions, although major leaks may pose the hazards of explosions and asphyxiation.

Crude Oil and Product Storage

Large tanks are used to store crude oil and refinery products prior to transport or use. Tanks may be located with production sites, pipelines, terminals, refineries, tank farms, or usage locations. The filling and emptying of storage tanks may result in the release of hydrocarbon emissions. A 1976 survey identified 25,000 storage tank locations (Petroleum Extension Service 1978). There are approximately 40,000 tanks with capacities greater than 40,000 gallons (151,000 liters). Annual volatile organic compounds (hydrocarbon) emissions from these tanks are estimated at 8.3×10 kilograms per year, or approximately 1.8 billion pounds per year. About 83 percent of these emissions are from tanks with fixed roofs and 17 percent from tanks with floating roofs which minimize emissions, as will be described below.

In 1976, the estimated ratio of fixed-roof to floating-roof tanks was about two to one, but the total capacities of both types were approximately equal. Recent regulatory actions will change this ratio, increasing floating-roof tank storage. For both tank types, the majority of hydrocarbon emissions were from tanks storing gasoline and crude oil. Hydrocarbon emissions from these tanks are shown in Table 2.

Fixed-Roof Tanks

Fixed-roof tanks provide the simplest and least expensive kind of aboveground bulk storage. They basically consist of a cylindrical steel shell topped by a hemispherical roof. They are generally equipped with a pressure/vacuum vent designed to minimize minor, pressure-induced outflows of hydrocarbon-laden vapors and inflows of air.

Vapor pressure changes that result in hydrocarbon vapor emissions are caused by a number of factors. Tank loading can cause vapors above the liquid surface to be displaced into the atmosphere. Evaporation, a constant process from the surface of any liquid, results in pressure buildup and eventual emissions. Solar heating of tank contents and the resulting expansion of vapors causes emissions. Heating may result from hourly, daily, or seasonal temperature changes. Tank "breathing" is a diurnal phenomenon that results in considerable emissions; heat from sunlight impacts on tanks, resulting in expansion and emission of vapors. Then cooling at night draws in fresh air, which increases vapor pressures, causing emissions as it becomes saturated with hydrocarbon vapors. Emission controls for storage tanks involve minimizing vapor spaces, tight sealing, reflective paints, and vapor recovery.

Floating-Roof Tanks

Floating-roof tanks minimize vapor losses by constantly minimizing vapor spaces. As the name implies, the roofs of these tanks actually float on the surface of the stored liquid. (They are not used for gas storage.) The roof rides up and down inside the tank shell as the oil level changes. Emissions from floating-roof tanks can be 95 percent lower than those from fixed-roof tanks. A fixed-roof storage tank may be made into a floating-roof tank with the internal installation of a floating roof.

Floating-roof tanks may be open (uncovered) or covered--essentially a floating roof within a fixed-roof tank. They may vary in their complexity, cost, and degree of emissions control. Major types of roofs include: simple floating decks consisting of a flat metal plate with a vertical rim and bracing for rigidity, decks with

TABLE 2

ATMOSPHERIC EMISSIONS FOR A FUEL OIL REFINERY MODULE^a
(lbs/day)

	Particulates	SO _x	CO	Hydrocarbons	NO _x
Crude distillation	3,080	6,400	533	533	5,300
Gas oil hydrotreater	280	539	90	128	1,084
Naphtha hydrotreater	19	27	16.2	27.7	219
Heavy naphtha reformer	1,960	4,073	340	340	3,390
Propane deasphalting unit	474	673	49.6	84.8	680
Deasphalted oil hydrotreater	30	42	25.2	42.9	340
Tail gas treating	3.4	3,410*	3.0	4.9	39
Light ends recovery	2.6	3.7	2.2	3.8	30.4
C ₅ /C ₆ isomerization	120	250	21	20.8	208
Storage					
Crude	---	---	---	7,550	---
Motor gasoline	---	---	---	3,730	---
Light fuel oil	---	---	---	564	---
Heavy fuel oil	---	---	---	Negligible	---
Sludge incineration	354	597	125	41	510
Miscellaneous emissions	---	---	---	60,900	---
Total	6,320	16,000	1,200	73,970	11,830

^aBased on 200,000 bbl/day crude feed.

*Mainly due to the tail gas itself.

pontoons around the rim to provide additional floating stability under heavy loads of water and snow, and double-deck roofs that employ two interspaced decks above the liquid surface. Double-deck roofs provide insulation between the top surface exposed to the sun and atmosphere, and the bottom surface covering the oil, thus providing thermal insulation and minimizing evaporation. Various types of seals are employed around the edge of the floating-roof deck to maintain vapor sealing and to permit raising and lowering of the roof.

Besides lowering vapor emissions, floating roofs perform a number of other functions. Fire hazards are reduced since vapors are minimized and the oil surface is almost entirely covered. Corrosion due to vapors rising from sour crudes, such as hydrogen sulfide, are kept to a minimum as their area of air contact is minimized.

Floating roofs still require pressure and vacuum release vents and produce evaporative and breathing emissions, but these are minimized due to the decreased vapor space.

Floating-roof tanks may be covered. In fact, covers may be required in some climates due to heavy rain or snow. Space between the fixed and internal floating roofs must be vented to prevent formation of explosive vapor concentrations.

Other Tank Types

Variable vapor space tanks are equipped with expandable vapor reservoirs to limit vapor volume fluctuations due to temperature, barometric, and pumping-induced changes. A variable vapor space tank normally is connected to the vapor spaces of more than one tank, usually fixed-roof tanks. The two most common variable space tanks are lifter-roof tanks and flexible-diaphragm tanks. Lifter-roof tanks have a telescoping, sealed roof that fits around the outside of and over the main tank wall. Local natural gas supplies are frequently held in simple tanks called gasholders.

Special Purpose Tanks

Pressure tanks, designed to withstand relatively large pressure variations without vapor loss, are generally used to store highly volatile refinery products. These tanks are typically spherical or cylindrical in shape and may withstand pressures up to 265 psia.

Underground Storage

The storage of oil underground is a recent activity. One of the goals of the Strategic Petroleum Reserve System as established by the

Energy Policy and Conservation Act (PL 94-163) is to have 150 and 500 million barrels of petroleum in underground storage (salt domes and salt or limestone mines) by December 1980 and 1982, respectively. Ultimately, the Department of Energy plans to store up to 1 billion barrels of crude oil in caverns created under Louisiana and Texas. The amount entering storage has fallen short of anticipated goals as a result of price and supply complications. A recent testing of withdrawal capability exceeded design rates at three storage sites.

The proposed caverns are expected to be produced by dissolving subterranean salt deposits with water. The dissolved rock salt forms a saline solution of about 265 parts of salt per 1,000 parts of water with a temperature range of 81° to 99°F (27° to 37°C). The process appears feasible wherever adequate water supplies and brine disposal conditions exist. (Brine disposal at inland sites may result in severe damage to terrestrial biota and upland soils.) The National Oceanic and Atmospheric Administration (NOAA) is evaluating the environmental impact of pumping saturated brine into the Gulf of Mexico's coastal waters. The study includes site-specific assessments and the development of a monitoring plan for brine discharges (Flagg 1980).

To date, the focus of attention on underground storage has been on safety problems as a result of an explosion and subsequent fire during filling operations at a Gulf Coast salt dome. Environmental concern has focused on impacts of the construction phase on wetlands as a result of the truck transport of materials, ditching, dredging, spoil stowage, and road and stream crossings causing noise, dust, mud, exhaust emissions, stream turbidity, and stream bottom disruption in pristine areas. Concerns over operations have focused on the permanent change in groundwater movement and the encroachment on and injury to local animal and plant species.

Underground oil storage is an area that should receive research attention since it is related to many national policy issues as well as to several facets of the oil and gas industry. For example, the proposed Northern Tier Pipeline, the survivor in the competition to move Alaskan North Slope crude oil from the West Coast to midwestern U.S. markets, is currently arranging financing for and acquiring the remainder of its permits to build the 1,557-mile pipeline from Port Angeles, Washington, to Clearbrook, Minnesota. One of the selling points of the project is that the route crosses the Williston Basin, an area with deep lying salt deposits along the Montana-North Dakota border. For several years the Northern Tier Pipeline Company has indicated that these deposits could be utilized for an inland strategic oil storage area served by the pipeline.

HEALTH AND ENVIRONMENTAL EFFECTS

Health and environmental effects associated with oil and gas transportation and storage are discussed in this section. The issues are categorized by the major facets of technology that have received attention as sources of potentially damaging emissions. The health effects of one group of pollutants--hydrocarbons--are not discussed in detail here. Humans are exposed to hydrocarbons at various points in the movement of oil, but much of the information on this subject is presented in the Refinery Operations section.

Marine Terminal Operations

Nearly all foreign and Alaskan crude oil is transported by marine tankers and barges, as is much of the oil produced in the lower 48 states. Crude oil is typically held in bulk storage facilities and pipelines at terminals or port facilities both before and after shipping. Refinery products frequently are also shipped by sea. Ship transfer--both the loading and unloading of crude oil and refinery products--may pose serious health, safety, and environmental hazards.

Marine terminal emissions generally have been unregulated. This lack of regulation is, in part, due to an unclear legal authority over the operations of ships while they are in port and underway. The tanker captain, Coast Guard, Environmental Protection Agency, and local or state authorities have varying interpretations as to their respective authority over different ship operations.

Tankers transporting oil between ports in the U.S. are subject to the Merchant Marine Act of 1920, commonly known as the Jones Act. This act requires that movement between domestic ports be carried out by U.S. built and owned tankers operating under the U.S. flag with American crews and masters. Coast Guard regulations implementing the Ports and Waterways Act of 1972 require vessels larger than 70,000 dead weight tons (dwt) to have segregated ballast tanks, two slop tanks (for retention of tank washings and oil residues), and an oil residue tank for the containment of oil leakages and sludge. Oil spills, ship collisions, discharge of water used for hydrostatic testing and cleaning, flushing of ballast tanks, discharge of bilge water and sewage, and other ship operations may result in intentional and accidental air and water pollution.

Most hydrocarbon emissions in or near port are associated with tankers that do not contain inerting and segregated ballast systems. A majority of these vessels are small (less than 75,000 dwt in size). Owing to their shallow draft, many U.S. crude oil importing ports are

served only by these unregulated small tankers which supply 60 percent of imported crude to U.S. coastal ports, mostly to the major crude importation areas of the East and Gulf coasts.

Many factors affect the magnitude of crude oil and refinery product transfer emissions. Adequate emission factors or correlations for estimating these hydrocarbon transfer emissions are difficult to develop due to the many ship, cargo, and operating variables involved (Burklin et al. 1976). Considerable work has been performed toward assessing emissions and other environmental concerns involved with the tanker transport of Alaskan crude oil to West Coast ports, primarily in the already hydrocarbon-polluted Los Angeles area.

Estimates based on the SOHIO project, a proposed (now terminated) major terminal for handling Alaskan crude (involving approximately 270 tanker visits per year), indicate that yearly SO_x emissions could range from 220 tons per year to 880 tons per year. These ranges are based on differences in fuels, particularly the sulfur content (0.5 to 2 percent). If transit time in the port vicinity is included, this range could be from 500 to 2,000 tons per year. NO_x emissions were estimated to range from 120 tons per year to 210 tons per year, depending on whether transit time is included. Carbon monoxide and particulate emissions were minimal and have not been an issue (airborne particles were estimated to be 40 tons per year; CO emissions generally were not calculated). One scenario of estimated emissions, compared with emission levels that define "major" air pollution sources,* is shown in Table 3.

Marine terminal emissions are primarily associated with loading and unloading operations. Loading emissions may be separated into an arrival and a generated component. The arrival component of loading emissions consists of displacement venting of hydrocarbon vapors left in empty cargo compartments from previous cargoes. The generated component consists of hydrocarbon vapors formed in the cargo tanks as liquids are loaded. The quantity of hydrocarbon vapors generated during loading depends on the vapor pressure of the hydrocarbons and loading practices, especially loading rates.

Loading Emissions

When a vessel arrives in port, prior to loading or unloading operations, hydrocarbon vapor concentrations typically are uniform throughout the compartment's vapor space. Upon arrival, a compartment in a gasoline loading vessel characteristically contains from 0

*Facilities categorized as "major" air pollution sources would be subject to offsetting requirements.

TABLE 3

YEARLY EMISSIONS FROM ALASKAN CRUDE
TANKERS AT PORT OF LONG BEACH

Pollutant	EPA Guidelines ^a (tons/year)	Estimates from SOHIO Project (270 visits/year) ^b	
		Port Only	Port & Transit
Particulates	50	40	60
SO _x	50	220 ^c -880 ^d	500 ^c -2,000 ^d
NO _x	50	120	210
HC	50	0 ^e -7,000 ^f	0 ^e -10,000 ^f
CO	500	Negligible	

^aGuidelines for defining a "major" source in effect at the time of SOHIO (Alaskan crude) environmental impact statement review.

^bOnly large tankers considered (100 visits, 80,000 dwt; 73 visits, 120,000 dwt; 97 visits, 165,000 dwt).

^cAssumes a fuel sulfur content of 0.5 percent.

^dAssumes a fuel sulfur content of 2.0 percent.

^eNo ballasting or tank cleaning (purging) assumed.

^fBallasting and tank cleaning (purging) assumed.

to 20 percent hydrocarbons by volume, but the proportion can exceed 50 percent hydrocarbons by volume (Burklin 1976). During loading, a vapor blanket two to eight feet thick, containing a high concentration of hydrocarbons, forms above the liquid surface. The generated component of loading emissions, this vapor blanket is primarily attributable to evaporation and turbulence of the input liquid. For vessels such as barges, which have shallow compartments (on the order of 12 feet), loading will cause the venting of the dense vapor blanket, producing proportionately more hydrocarbon emissions than the loading of tankers that have deeper drafts (on the order of 55 feet), unless the last few feet of compartment depth is filled. Loading-generated, turbulence-induced, vapor blanket depth may be significantly reduced--up to 50 to 60 percent--by slow initial loading. Cleaned and vented tanks (lacking an arrival vapor component), which are initially loaded slowly and not filled to the top, will produce minimal emissions. Slow final loading can lower hydrocarbon emissions due to less disturbance and venting of the vapor blanket.

The true vapor pressure (TVP) of a hydrocarbon liquid has a marked impact on the hydrocarbon content of its loading and unloading emissions (Burklin 1976). TVP is an indicator of volatility and is a function of the liquid's Reid Vapor Pressure and temperature. High TVP liquids have high evaporation rates (high volatility) and produce high hydrocarbon concentrations in loading and unloading vapor emissions. The TVP of crude oils can range from 0 to over 15 psia and the TVP of gasolines may range from 6 to 10 psia.

Many different estimates for port hydrocarbon emissions have been developed, based on different assumptions of what tanker operations are performed in port or at sea. Limited barge emissions data indicate that hydrocarbon emissions are in the range of 27 percent by volume. Hydrocarbon concentrations in emptied crude oil tanks may reach 10 percent by volume, but are more typically in the 5 percent range. Actual concentrations depend on a number of factors, including the TVP and volatility of the crude oil, mixing time, and turbulence. For emptied gasoline tanks, vented vapors may be within the explosive concentration range, typically 1.4 to 8.4 percent by volume, during most of the loading operation. Vented vapors may pose explosive hazards, besides adding to the ambient hydrocarbon concentrations in the vicinity of the port and at sea.

Tankers in port produce considerable emissions besides hydrocarbons. A ship's boilers are rarely shut down while it is in port, so there are combustion-related emissions that result from hotelling or idling at the pier, pumping and ballasting operations, maneuvering to dock, and the maintenance of many of a ship's systems. It is believed that tankers in berth burn more fuel than other ships of similar size, as on-board pumps are used to unload crude and refinery

products. Offloading involves using the tanker's on-board engines at 80 percent of full power for 10 to 12 hours for tankers in the 80,000 to 165,000 dead weight tonnage class. The sulfur content of the fuels that tankers use may vary and, even ignoring these variations, sulfur oxides and other available emissions estimates vary greatly. Tanker hydrocarbon emissions from fueling and boiler combustion are negligible compared to those from transfer operations.

Tanker purging, ballasting, venting, and storage tank emissions are the major sources of hydrocarbon emissions from crude and refinery product marine transfer operations. The present operating practices, frequency of occurrence, and levels of emissions and emission controls associated with these and other transfer operations are unknown.

Emission controls for marine tanker and barge operations involve basic design features and operating practices. Significant hydrocarbon emissions from oil tankers and barges result mainly from the displacement of hydrocarbon-laden air from empty storage compartments and from the operation of a ship's internal combustion engines. Various sources of marine transfer emissions and their control measures are discussed below.

Ballasting

Ballasting involves filling empty cargo space or segregated, dedicated ballast tanks with seawater after discharging cargo. Ballast is required to ensure proper ship seaworthiness, stability and balance, trim, and propeller immersion. The amount of ballast taken on depends on a number of factors, including the vessel's route, displacement characteristics and proportions, and expected weather conditions. Normally, from 15 to 20 percent of the vessel's total cargo carrying capacity may be taken on as ballast in port. Once at sea, cargo-empty vessels take on additional ballast to approximately 40 percent of their total cargo capacity.

Conventional tankers take on ballast in three alternative ways:

- o All necessary ballast is taken on in cargo tanks (with the minor exception of fore and aft peak tanks).
- o A portion of the necessary ballast is taken on in segregated ballast tanks, and the remainder is taken into cargo tanks.
- o All necessary ballast is taken on in segregated ballast tanks.

The majority of tankers in world trade do not have 15 to 20 percent of their capacity devoted to segregated ballast tanks; thus, initial ballasting is largely accomplished in cargo compartments in port. U.S. Coast Guard regulations and the Inter-Governmental Maritime Consultative Organization recommend that new tankers of 70,000 dead weight tons or more be required to have fully segregated ballast tanks equal to about 35 percent of capacity.

Taking on ballast displaces hydrocarbon vapors present in previously unloaded cargo tanks, much the same as does the loading of crude oil or refinery products.

Inerting Systems

Vapor spaces in cargo compartments carrying crude oil or refinery products contain potentially explosive concentrations of hydrocarbon vapors and air containing oxygen. Inerting systems pressurize the vapor space of cargo compartments with oxygen-poor flue gas from the ship's boilers. Exhausted flue gases are passed through a scrubber where they are cleaned and cooled before they are vented into the cargo tanks. During this process, approximately 17 percent of the flue gas is diverted from entering the atmosphere, which reduces total stack emissions proportionately for tankers in the 120,000 to 165,000 dead-weight-tonnage class. During loaded passage, the inert atmosphere above the cargo liquids is maintained by periodic repressurizing. When oil is offloaded, inert flue gases are pumped into the tanks as oil is pumped out to ensure that the tank's atmosphere remains inert. Besides eliminating explosive hazards, such inerting systems reduce corrosion in cargo compartments.

When cargo-empty inerted compartments are loaded, the flue gases are displaced and exhausted, along with some hydrocarbon vapors from evaporating fluids that remain on the sides and bottom of the compartments.

Gasfreeing

Empty and ballasted cargo compartments may be purged of their hydrocarbon-laden atmospheres by replacement with air. Air may be blown in (purging) or cargo compartment covers removed (venting). If empty tanks have previously been washed thoroughly at sea, the gasified tanker may take on cargo without venting hydrocarbons in port, or workers may enter the compartments for maintenance. Significant hydrocarbon emissions may occur in port if gasfreeing operations are performed there.

Compartment Washing

Emptied cargo compartments contain hydrocarbon liquids that lie in residual puddles and wet the side walls. Tank walls and floors are usually washed down with water before a new cargo is loaded. A recent practice is to wash with crude oil, thus eliminating a potential water pollution problem. Residual hydrocarbon liquids in the cargo compartment, with or without washing, volatilize to form the empty cargo compartment's vapor component. Compartment washing may significantly reduce the concentration of hydrocarbon vapors in the tanks upon arrival, subsequently decreasing hydrocarbon emissions upon loading. Liquids from washing usually are stored in slop tanks for disposal onshore, often in a refinery wastewater treatment system.

Emission Control

Emission control technology for marine loading is a young technology with a unique set of problems (Burklin et al. 1976). A ship's hydrocarbon vapors are exhausted at high rates and frequently contain air, presenting an explosive hazard when handled by any type of machinery. The cumulative loading rate for a gasoline tanker can be as high as 50,000 barrels (210,000 gallons) per hour--equivalent to 4,700 scfm of displaced vapors.

Vapor control technology used for truck loading is not directly applicable to marine terminals, because hydrocarbon vapor concentrations in tank truck loading are above the explosive range and the rates of vapor displacement are much lower. Some control technologies currently available include vapor collection and condensation at cryogenic temperatures (-80°F to -100°F), absorption in a refinery oil stream, and incineration or flaring of vapors. All of these methods pose additional hazards and considerable expense. The first two methods do not remove methane vapors. Vapor dilution or saturation, required in most systems to avoid handling vapors in their explosive concentration range, is energy-intensive.

Storage Tank Operations

Vapor emissions from storage tanks result from the following:

- o Fixed-roof breathing losses--due to thermal expansion of vapors, vapor expansion caused by lowered atmospheric barometric pressures, and increases in vapor due to liquid evaporation.
- o Fixed-roof working losses--due to vapor expelled from tanks as a result of filling and emptying operations. (Emptying

loss is attributable to subsequent vapor pressure increases as newly inhaled air becomes saturated with hydrocarbons.)

- o Floating-roof standing storage losses--due to improper fit of roof seals.
- o Floating-roof working losses--same causes as fixed-roof working losses, but amounts emitted are significantly less.
- o Floating-roof withdrawal losses--due to evaporation from wetted tank walls as tanks are emptied. The loss is small in comparison to other loss types.
- o Variable space filling losses--due to loss of vapors upon filling when expandable storage capacity is exceeded.
- o Pressure tank losses--due to relief venting when operating pressures are exceeded. This is not a significant source of emissions under normal operating conditions.

The amount of evaporation and other losses from storage tanks depends on a number of factors, including:

- o True vapor pressure of the stored liquid;
- o Temperature changes in the tank;
- o Height of the vapor space;
- o Tank diameter;
- o Schedules of filling and emptying;
- o Mechanical condition of tanks and seals;
- o Type of tank and paint applied to outer surface; and
- o Fugitive emissions due to vapor and/or liquid leaks.

Equations to estimate tank vapor losses have been developed, but have not been extensively field tested or universally accepted.

Vapor recovery systems are the major emissions control technology appropriate for the recovery of vapors exhausted from storage tanks. These are not as widely used in refineries as floating-roof tanks, probably due to their high cost and energy requirements.

Tank Safety

Fire walls are required around storage tanks holding flammable liquids. These dikes, at least equal in capacity to the storage tank they surround, are designed to hold a tank's contents in case major leaks or spills occur. Besides holding oil for recovery, fire walls prevent the spread of burning oil to adjacent tanks and buildings. Sometimes, but rarely, safeguards may break down, allowing spilled oil to enter stormwater runoff drains. When this occurs, a catastrophe could result.

When ignited, light refined oil products usually burn quietly until extinguished or burned dry. Crude oil, heavier refined oils, and fuel oils are liable to boil over after burning for some time in the tank. Boiling over results when heat from the burning surface works its way down to the bottom layer of water present in nearly every tank. The water layer flashes into steam, expelling burning oil out of the tank.

Numerous mechanical safeguards and operating procedures are employed within the oil industry to maximize safety in case of human error, fires, explosions, ground settling, earthquakes, and other mishaps that inevitably may affect storage tanks.

Design Trends

Recently, new standards concerning storage tank technology and emissions control have been promulgated (Federal Register 4 April 1980). These standards, designed to limit volatile organic compounds (hydrocarbons) emissions, apply to new, modified, or reconstructed petroleum liquid storage vessels with a capacity for more than 40,000 gallons (151,000 liters) of liquids with a true vapor pressure greater than 1.5 psia (10.3 kPa). These regulations require either the use of double seals on external floating roofs, a seal on internal floating roofs, a vapor recovery and disposal or return system that reduces emissions by more than 95 percent (by weight), or any equivalent, demonstrated emissions control method. Most crude oils and refinery intermediates and products are covered by these regulations. Storage vessels used in crude oil extraction operations and those with a capacity of less than about 420,000 gallons (1.6 million liters) are exempt. Petroleum product tanks are covered by the regulations, wherever their location, including those in chemical plants.

Pipeline Gas Processing

Accidents occur more frequently in natural gas operations than in corresponding crude oil operations. However, natural gas

operational accidents generally cause far less environmental damage. Accidents include gas well blowouts, gas gathering line leaks, and malfunctions of gas processing equipment.

No substantial amounts of water or solid waste contaminants are released during gas gathering or separation. The major environmental impact relates to air quality. The estimated emission level of nitrogen oxides during gas gathering is 2.6 tons per 10^{12} Btu's gathered. This is derived from the use of 3.7 percent of the produced fuel in gas engines used to drive compressors. The level represents over 55 percent of all nitrogen oxides emissions associated with the extraction, gathering, and processing of natural gas.

Nitrogen oxides emissions pose problems for health and the environment (e.g., acid rain). For discussion of effects and research needs associated with nitrogen oxides emissions related to natural gas (mostly emanating from compressors), see the End Use section of this report and the Report of the Interagency Task Force on Environmental Issues (U.S. Department of the Interior 1977).

Air emissions associated with sulfur removal are small--amounting to about 0.4 tons per 10^{12} Btu's of gas processed (based on processing 60 million cubic feet per day). About 70 percent by weight are nitrogen oxides. The emissions are a result of using natural gas as a fuel to produce process steam. Elemental sulfur, produced in this process, can be marketed and is not considered to be a waste material.

Based on a plant processing 60 million cubic feet per day of a gas containing one grain of hydrogen sulfide per standard cubic foot of gas, about 0.8×10^9 Btu's per 10^{12} Btu's of natural gas processed is released in the water effluent. This thermal enrichment is about 1/10th of the amount released from a natural gas liquids processing plant (University of Oklahoma 1975).

Because of the danger to operating personnel, field procedures for sour gases must include precautions not required in the production of sweet gas. Safety measures have been developed to cope with this long-recognized problem.

Gas Pipelines

Almost all pipeline accidents can be attributed to corrosion damage by outside forces, construction defects, or material failure. Corrosion may be internal or external. External corrosion may result from the chemical and electrolytic salt action of water, groundwater, soils, and sediments. Internal corrosion is caused by hydrogen sulfide, water, or acidic conditions. External corrosion is lessened

with coatings, cathodic protection, and the use of corrosion resistant materials such as plastic, aluminum, and stainless steel. Internal corrosion is lessened by interior coatings, injecting corrosion inhibitors, and chemicals. Chemicals include oxygen scavengers to reduce dissolved oxygen concentrations, dehydrants, and bases.

Gas pipeline accidents tend to affect non-employees rather than employees of pipeline companies (Table 4). Examples can illustrate the accidents which may occur. In Bainbridge, Georgia, on August 26, 1976, a two-inch steel pipeline was damaged. It had an open end and inadvertent opening of a valve permitted gas to escape. The gas migrated under pavement and into a post office. An explosion and fire resulted, killing one person in the post office and injuring two others. In Hugo, North Carolina, on September 29, 1975, three fatalities occurred from a fire and explosion resulting from the escape of natural gas into an air-conditioning control room. The accident was traced to the weight of a sewer line causing a split in polyethylene service line carrying 45 psig 12 feet from the building (Bliss 1977).

Pipeline Spills

This section considers the potential effects of terrestrial oil spills resulting from the pipeline transport of crude and refined petroleum products. Some emphasis will be placed on northern and arctic areas. There, the construction and operation of the Trans-Alaska Pipeline has resulted in much preliminary information being made available. The discussion will include a consideration of the potential effects from both liquid and gaseous components. Where possible, the impacts of combusted petroleum on plants and animals also will be considered. Because petroleum fires may accompany large spills, this area would also seem to merit some consideration. The approach taken here will be to consider how an ecosystem's microorganisms, plants and animals may be impacted by petroleum. It should be emphasized that potential ecological effects of any petroleum spill will be subject to many variables, and that the extrapolation of results from one terrestrial system (e.g., the arctic) to another requires caution. Among such variables are the:

- o Type and quantity of oil spilled,
- o Location of the spill,
- o Topography of the area,
- o Single or repetitive spills,
- o Season of the year,

TABLE 4
SUMMARY OF GAS PIPELINE ACCIDENTS AND CASUALTIES

Calendar Year	Distribution					Transmission and Gathering				
	Number of Failures	Fatalities		Injuries		Number of Failures	Fatalities		Injuries	
		Employees	Non- Employees	Employees	Non- Employees		Employees	Non- Employees	Employees	Non- Employees
1970	676	1	20	32	170	343	1	0	8	8
1971	875	6	36	36	329	410	2	1	14	10
1972	884	2	26	32	262	409	3	3	23	13
1973	893	1	32	48	285	471	1	1	3	16
1974	1,017	1	19	31	283	460	1	3	7	13
1975	979	0	8	29	191	394	5	1	8	9

Source: Bliss 1977.

- o Type of soil,
- o Life stages of impacted organisms,
- o Metabolic rates of organisms, and the
- o Mobility of organisms.

This list is not meant to be inclusive, but only representative of factors that can change from one area to another.

Microorganisms

Crude Oil. Bacteria and fungi are responsible for both the degradation of organic matter and the concomitant recycling of nutrients. As such, they play a vital role in all terrestrial ecosystems. Various investigations have been carried out to discover how petroleum may affect both the population dynamics and physiological functions of these organisms. In this context, Sparrow et al. (1978) studied the response of microorganisms to crude oil spills on sub-arctic soil. These were short-term experiments carried out over summer and winter. The research was designed to determine how crude oil spilled during different seasons would affect soil microorganisms. Hot crude oil (7,570 liters) was applied to each of two (10 by 50-meter) plots. One application was made during winter, the other during summer; and no oil was applied to a control plot. Following the winter application there was a marked difference in the way the fungi and bacteria responded to the oil. The number of fungi declined while the bacteria increased in number on the oiled plot compared to the control. After the summer application even greater numbers of bacteria were present on the oiled plot compared to the control. The number of fungi still showed either lower or approximately equal numbers of organisms. This remained the case until September when the fungal count rose to five times that of the control plot.

In another project designed to study the response of soil fungi to oil, similar inhibitory responses were noted (Miller et al. 1978). In this 3-year study, oil was applied to experimental plots at 5 and 12 liters per m². The treated plots were compared to unoiled control plots. Fungal biomass was significantly less in both oiled plots over all 3 years. Furthermore, no difference was detected between the two levels of oil in this response. In addition to fungi, other groups of microorganisms have been found to respond to applied oil. It also has been reported that denitrifying, proteolytic, and cellulose-utilizing organisms may actually be stimulated by the presence of oil (Sparrow et al. 1978).

Longer-term studies have been carried out on microbial response to crude oil. Sexstone et al. (1978) examined the effects of crude oil at Barrow, Alaska, on microbial populations 2 and 7 years after oil was applied to experimental plots. They also attempted to correlate the relationship of various soil parameters to interactions between petroleum and microorganisms. The experimental plots were designed so that a gradient of soil moisture existed within them. In those plots that were studied 2 years after the application of crude oil, a general increase in microbial numbers was observed in all plots except for those with wetter, less well-drained soil. Residual oil was found in soil from both the 2- and 7-year-old plots, with the greatest concentration found at the surface (zero- to two-cm) level. In the well-drained soil plots, some oil was detected throughout the entire zero- to eight-cm cores of soil. In the wetter, less-well-drained soil, oil remained much closer to the surface. In general, it was found that oil remained at or relatively near the soil surface, and that oil reached its maximum soil penetration within 1 year of application. Evidence that microbial degradation of the applied oil was slowly taking place was inferred from column chromatographic studies. However, no evidence was gathered in this particular study which demonstrated that specific classes of oil hydrocarbons were being preferentially degraded by microorganisms.

Diesel Oil. In another geographic area with different soil topography, another study (Sexstone et al. 1978) analyzed the results of both controlled crude and refined (diesel) oil spills. The numbers of hydrocarbon-utilizing microorganisms were found to increase in the wetter soils in plots treated with both crude and refined oils. These results differed from those obtained in the former study, where wetter soil had relatively fewer organisms than did drier, better-drained soil.

Mycorrhizal Fungi. The impact of oil on soil microorganisms extends beyond its effect on relatively simple, free-living organisms. What must also be considered are the effects that petroleum may have on symbiotic microorganisms. Mycorrhiza are a widespread and important group of such organisms. The word mycorrhiza literally translates as "root fungus." These fungi are extremely important to the plants with which they are associated. It is through such fungi that nutrients which nourish plants must first pass. The potential impact of a petroleum spill on such microbial-plant associations could be large and potentially as severe as a marine oil spill.

Preliminary studies on the effects of crude oil on such symbiotic fungi have been carried out. Antibus and Linkins (1978) examined the effects of crude oil on such a fungal deciduous shrub association over a 3-year period. Changes in both anatomical structure and the number of viable mycorrhizae were found. There was an especially

large reduction in the number of viable mycorrhizae after the first week the oil (12 liters per m²) was applied. It was reported that after this high initial response, destruction continued, but at a slower rate throughout the remainder of the growing season. Three seasons later, the effects were still apparent.

The effects of oil on mycorrhizal-root respiration have also been investigated. Antibus and Linkins (1978) studied the effects of 5- and 12-liter per m² applications of crude oil on the shrub Salix rotundifolia. Within 48 hours after the application of oil, respiration for the 5- and 12-liter per m² plots was depressed by 22 percent and 56 percent, respectively. Respiration values remained depressed (below controls) for the remainder of that summer. The following summer, respiration rates for the 5-liter per m² plots were above controls, while the 12-liter per m² plots were still 20 percent below controls. The third and final summer found little difference in respiration between the treated and control areas.

Methanol. In addition to terrestrial effects that may result from accidents in petroleum pipeline transport, there are potential effects involving the chemicals used to initially test pipelines. Methanol is one chemical that has been strongly proposed for use in hydrostatic pipeline pressure testing. The conversion of natural gas (methane) into methanol for ease of transport has also been proposed. There have been few in-depth studies conducted on the potential effects of such a spill on soil microorganisms and the concomitant persistence of methanol in soil. Bryant (1975) reported the results of laboratory studies in which varying amounts of methanol were applied to soil cores. Both absolute and 20 percent methanol solutions were used for these experiments (distilled water served as a control). It was reported that 20 percent methanol had an immediate effect on soil bacteria, causing an overall decrease in bacterial numbers; however, 1 week later the population had recovered and no dramatic population shifts were observed. When absolute (100 percent) methanol was applied to soil cores, a more sustained effect on bacterial numbers was noted, as well as some population shifts. In another study (Parkinson 1974) in which 20 percent methanol was applied directly to field plots at varying rates, greater bacterial numbers were found in the methanol plots than in the control plots. Fungal response to methanol was also noted; however, no significant difference was found in the total number of species. Field samples from treated plots were examined for the possible persistence of methanol, but none was detected.

Vapor Phase Organics. In addition to the effects from liquid petroleum or microorganisms, are those that may result from petroleum associated vapor emissions. For example, vapor phase organics may affect soil fertility by inhibiting the germination of spore forming

bacilli that are common to fertile soil. Such a spore inhibiting effect has been demonstrated for many vapor phase organics, including: propane, n-butane, propylene, 1-butene, trans-2-butene, 1,3 butene, 3-methyl-1-butene and isobutane (Rode and Foster 1965). In experiments with spore suspensions of various species of Bacillus, it was found that spores remained dormant under a butane atmosphere, but germinated after the gas was removed (U.S. Environmental Protection Agency 1975). Not all vapor phase organics have such an effect. For example, some of the more important petroleum associated organics (e.g., methane and ethane) have not been shown to cause this inhibiting effect. In addition to spore inhibition, other effects on soil microorganisms also have been shown to result from exposure to various hydrocarbons. For example, Koike (1961) examined the effects of various hydrocarbons on the soil microflora and found that some compounds significantly retard soil nitrification. Other investigators have shown that some halogenated hydrocarbons had more effects on bacteria than fungi (Wensley 1953). Such interactions between hydrocarbons and microbes could disrupt a sensitive balance within soil ecosystems.

Upland Vegetation

Crude Oil. In addition to impacts on soil microorganisms, petroleum and its constituent or derivative components (both liquid and gaseous) may also strongly affect terrestrial vegetation. Some potential disasters for soil and vegetation along the proposed (now terminated) crude oil pipeline from Long Beach, California, to Midland, Texas, have been identified. Not only could a major pipeline rupture result in serious soil and groundwater contamination in general, but this pipeline in particular would have crossed agricultural valleys and grazing lands such as San Bernardino, Palo Verde, and Casa Grande, as well as natural desert and prairie land. In agricultural areas, it was speculated that, if not removed or leached out after a major spill, oil might remain in the top two to three feet of soil, causing soil contamination and crop loss (U.S. Department of the Interior 1976). It was further noted that it might take a "few years" before aerobic soil microbes degraded the oil in such agricultural areas; and that soil and native vegetation in non-agricultural areas over which the pipeline crossed might take even longer periods to recover.

Direct experimental studies on the effects of oil and related compounds on vegetation also have been undertaken. Generally conducted in northern (e.g., Alaskan and Canadian arctic) regions, they have dealt primarily with the effects of such compounds on natural upland vegetation. A few studies have also considered effects on transitional ecosystems such as marsh lands. Hutchinson and Freedman (1975) studied the effects of crude oil on tundra vegetation in the

Canadian arctic. Both short- and long-term effects were recorded over a 3-year period and the crude oil was applied by two methods. In one, oil was evenly applied at a relatively low level (9.2 liters per m²). In the other, a point source spill of 50 barrels was employed. Both spills were reported to have had a devastating effect on vegetation with very little recovery even after the third summer. Lichens and mosses were almost completely eliminated. Oil was said to have acted as a "contact herbicide." Both chlorophyll and water metabolism appeared to be affected. Winter spills were reported to be less severe than summer spills, due to little foliage growth during the winter. Plant reproduction was severely affected whether the oil was applied in summer or winter. It was noted that few species had flowered or borne fruit 3 years after the spills.

Jenkins et al. (1978) analyzed the effects of crude oil spills on a specific vegetation type (black spruce) in Alaska. As in the former study, both summer and winter spills were employed. In both seasons, 2,000 gallons (7,570 liters) of crude oil were used. Oil was found to have flowed much farther in summer and covered a greater total area than in winter. Vegetation mortality was complete within those areas covered by surface flows of oil. It was reported that deciduous species had the most rapid injury, with evergreen species having a more delayed response. Where oil covered the surface, vegetation did not recover.

Linkins et al. (1978) also examined the effects of surface-applied crude oil on vegetation. They found that the rate of root respiration in higher plants was depressed more than a year after an initial application of crude oil with concomitant decreases in viable biomass noted over a 3-year period. It was suggested that the continued decline in biomass may indicate that, when roots are subjected to fresh or weathered oil, their ability to tolerate environmental extremes such as drought or cold is impaired.

Products. Other research has examined the effects of refined petroleum spills on northern vegetation and possible restorative measures. Hunt et al. (1973) found that vegetation affected by spills of various refined products such as gasoline responded well to revegetation when nitrogen and phosphorous fertilizers were applied. Their experimental plots showed both an increase in density of vegetation and in microbial activity. It was not determined if the increase in vegetation resulted from the fertilizer alone, or from an increased rate of microbial petroleum degradation.

Wetlands. In addition to studies on the impact of oil on upland vegetation, research has also been carried out on transitional emergent vegetation such as is found in marshes. Marshes, besides being

near coastal and inland waterways that are highly susceptible to navigational petroleum spills, may also be at risk from coastal and major inland pipelines.

The effect of oil on marsh vegetation is apparently severe. For example, crude oil that had surface contact with plants, such as sedges, horsetails, and mosses, has been observed to cause extensive chlorophyll loss and death to young plant shoots. On the other hand, it has been reported that plant parts which are below water level survive and emerge the next season (Hellebust et al. 1975). Another study, however, reported that there actually was greater net productivity in stands of *Spartina alterniflora* (a major marsh species) exposed to an oil spill than in control plots. In another study on a spill involving a lighter oil (no. 2 fuel oil), it was postulated that marshes were acting as a "sponge." The spilled oil was retained by the marsh and subsequently released over long periods of time (U.S. Environmental Protection Agency 1979). This persistence of a relatively light fuel oil for long periods of time disproves the frequently-stated assumption that light fuel oils are quickly dissipated in wetlands.

Evaporative and Gaseous Emissions

Petroleum-related gases and vapors, including those generated by combustion processes, may have varying effects on a plant community. Probably the most important of the petroleum-derived gas products transported through pipelines is methane, the major component of natural gas. When breaks occur in underground pipelines carrying this compound, local vegetation may be severely impaired. Various physical and chemical changes leading to plant deaths have been observed (Adams and Ellis 1960).

Probably of more direct concern are the reactions that hydrocarbon vapors and/or petroleum combustion products may undergo, and any adverse effect that may result. It is important to recognize that such gaseous pollutants may undergo reactions with each other, and with normal atmospheric constituents, to produce compounds that may have pronounced effects greater than those of the individual components.

Vapor phase compounds that may be classed as organic pollutants include a large number of organic compounds that are the result of incomplete combustion (partial oxidation), varying from almost a pure carbon to peroxyacetylnitrates (U.S. Environmental Protection Agency 1975). Such vapor phase organics, if arising from a large-scale spill, with or without an ensuing fire, may react with atmospheric components such as ozone, SO_x , and various nitrogen oxides (NO_x) to produce highly phytotoxic compounds. Such reactions are often of

a photochemical nature (i.e., catalyzed by sunlight), and have been extensively studied in urban areas such as Los Angeles where the pollutants are collectively termed "smog." It is not unreasonable to assume, in the event of a massive or multiple spill, that relatively large volumes of potentially reactive vapors may undergo similar photochemical transformations. This could especially be true of petroleum fuel fires.

The effects of urban smog on vegetation are well known and have been implicated in the injury of vascular plants. Three important, specific phytotoxic compounds have been identified: ozone, nitrogen dioxide, and peroxyacynitrate (PAN) (U.S. Environmental Protection Agency 1978). Peroxacylnitrates are the most phytotoxic of these known oxidants. Many studies have attributed plant symptoms resulting from smog to be directly due to PAN or its derivatives (Middleton 1961; Taylor 1969; Hershaft 1976).

The general effects of smog-induced injury have been reported as irregularly distributed bronzing or glazing on the bottom side of the leaf (Middleton et al. 1958; Middleton 1961). Plants exposed to PAN also develop distinctive characteristics including visible and internal metabolic changes such as chlorosis, necrotic streaking and stippling (U.S. Environmental Protection Agency 1975). Stephens and Scott (1962) have reported the development of lesions on sensitive petunia and tobacco varieties exposed to PAN. Similarly, noticeable effects have been reported for lima beans and corn.

Depending on such variables as the concentration of pollutants and the duration of exposure, increases in cell permeability and decreases in photosynthetic rates following exposure to PAN and ozone have also been documented (Tingey 1977). It has been speculated that other effects may include aberrant enzyme activity and changes in translocation of materials within plants.

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SUMMARY OF RESEARCH NEEDS

The following are research needs related to oil and gas transportation and storage.

Health

- o Because of the potential for dermal exposure to ethanolamine, toxic properties of the chemical should be studied more closely. It is considered a corrosive material, but its toxicity has not been established (Lewis 1979).
- o The potential for nitrosamine formation should be examined for areas where considerable amounts of ethanolamine are exposed to ambient air.
- o Safety procedures should be developed regarding public exposure to unguarded deep trenches during pipeline construction through urban areas.
- o A health risk assessment is needed with respect to the exposure of pipeline construction workers to coal tar pipe coatings, coal tar-saturated wrapping materials, and asphalt coatings and wrapping materials.
- o A set of guidelines should be developed to provide conformity in the assumptions used in determining emission factors for air quality analyses of proposed marine terminals. The guidelines would recommend approaches for scenarios involving the number of tankers in port simultaneously, the duration of such a condition, and the length of travel into port associated with air quality implications. The guidelines would provide common ground for the development of worst case, business-as-usual, and best case scenarios, as well as consequent emission factors for the evaluation of new port facilities.
- o There is a need for epidemiological studies of individuals involved in oil transfer operations. Loading and offloading operations can result in occupational exposure via inhalation and dermal contact.
- o Relating to the hazard of explosions and fires at terminal facilities, several measures can be taken during the construction or operation of tankers and their support facilities to eliminate or significantly reduce adverse impacts upon air quality in or near port locations. These include:

- o Ship or facility design--a minimum 35 percent segregated ballast capacity; controlled offshore mooring sites; and required inerting systems for cargo holds.
- o Control technology--the use of recycling flue gas scrubbers for all flue gas emissions(in place of once-through systems); requiring vapor recovery systems for terminal operations (in addition to storage tanks); continuous on-board monitoring of tanker emissions; and combustion modification processes.
- o Operations--requiring the use of low sulfur fuel (0.5 percent sulfur content or less); use of natural gas as an inerting medium; and curtailment of in-port purging or gas freeing.

The feasibility of implementing these options should be explored in depth. It is conceivable that ships, while non-mobile and tied up at a pier facility, may be considered stationary sources of emissions and may come under the jurisdiction of EPA under the Clean Air Act. The ramifications of this possibility should also be explored.

Environment

The following are research areas where additional information is needed, especially with respect to microorganisms:

- o More research on how oil may affect plant-microorganism symbiotic relationships (e.g., mycorrhizal-plant associations). This is an important research area which may provide useful data for the development of reclamation strategies.
- o Increased research on the effect of oil in different soil types; specifically, how do physical and chemical characteristics of a particular soil interact with petroleum to affect microorganisms? Can predictive indices on the effects of oil on microorganisms be developed using regional soil classifications?
- o More research on how crude and refined petroleum affects such basic microbiological processes as nitrification, denitrification, and soil nutrient cycling.
- o More study of the effects of oil on different populations of soil organisms. To what degree does oil affect bacterial versus fungal populations? What is the regeneration limit of major soil groups after exposure to oil?

- o Additional research on how vapor phase and gaseous hydrocarbons affect microbial dynamics and interactions. Such studies could be especially useful in understanding the terrestrial effects and subsequent reclamation procedures associated with underground pipe ruptures involving natural gas or other related petrochemicals.

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Part 7
End Use

END USE SUMMARY

This section lists numerous research needs related to human health. Of particular importance is the newly recognized problem of indoor air pollution. Recent research has found that combustion of oil and gas products in the home has led to potentially harmful indoor levels of nitrogen dioxide, carbon monoxide, and radon.

In addition to being pollutants themselves, nitrogen dioxide and other emissions from indoor oil and gas combustion also may compound the problems and reactions of indoor air pollutants. Nitrogen dioxide levels have been found to be significantly higher (in some cases seven times higher) in homes with gas stoves than in homes with electric stoves. Gas appliances have been cited as significant sources of carbon monoxide. However, air emission research has focused largely on air pollutants associated with the infiltration of automotive exhausts and on volatile solvents.

Research on indoor radioactive emissions has focused on radon emanating from construction materials and on water supplies derived from aquifers located in sedimentary deposits rich in radioactive nuclides. Evidence suggests the possibility of an equal amount of radon released from the combustion of natural gas in gas ranges and space heaters.

Various aspects of indoor air pollution are discussed at length here in the Technology Description section under Indoor Emissions, the Health Effects section under Indoor Air Pollution, and in the Summary of Research Needs relating to health effects and transport and transformation.

The nature, magnitude, and role of radioactive and chemical emissions from the indoor, energy-related use of oil and natural gas should be determined. Research in this area should be integrated with a comprehensive research program that addresses all facets of indoor air pollution.

A large number of research needs involve dermal and inhalation effects associated with human exposure to petroleum products and combustion gases. These highlight an overall need for an expanded research effort dealing with exposures from oil and gas retailing. This effort should focus on workers (e.g., gas station attendants), as well as the public using self service gasoline stations. The nature and magnitude of acid and alkaline metal emissions from catalytic converters needs to be fully explored with respect to both health and environmental impacts.

With respect to environmental effects research, additional research is seen as needed in the following areas: the biological transport of lead, cadmium, and nickel in soil and food chain accumulation; the landfarming of waste oils; and the effect of evaporative hydrocarbons from road surfaces on roadside flora and crops.

Several transport and transformation research needs are cited in this section. Some of the more important relate to photocatalytic processes that can convert innocuous hydrocarbons into polynuclear aromatic species; the role of organometallic emissions which may serve as catalysts, solvation agents, or forces responsible for sorption; interaction of coal fly-ash and condensed hydrocarbons; and the development of standardized and reliable techniques to characterize diesel engine exhausts that eliminate the formation of artificial compounds during testing.

END USE

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END USE

TECHNOLOGY DESCRIPTION

In the multifaceted oil and gas technology sequence, the final step (after onshore and offshore exploration and extraction, transportation and storage, and refinery operations) is end use. This section deals with oil and natural gas as an energy source used in the stationary and mobile combustion processes. It also touches on the use of petroleum oils as lubricants in gasoline engines, diesel engines, machines, and industrial applications, after first discussing the different types of fuels in use.

Types of Petroleum Fuels

Petroleum fuels are essentially mixtures of various hydrocarbons and different additives intended to improve quality or to counteract and reduce hazards associated with some of the hydrocarbons and their impurities. Because petroleum fuels are refined--or distilled from a broad range of feedstocks--they may be categorized by their end uses.

Gasoline

In the early days of the automobile, gasoline was a simple mixture of petroleum fractions derived from straight-run and thermally cracked stocks. The major chemical components were total saturates, 56.38 to 68.38 percent; total alkanes, 5.0 to 7.69 percent; and total aromatics, 24.32 to 32.91 percent. The percentages vary because of the different constituents in low-, medium-, and high-octane gasolines. The maximum sulfur content set by the American Petroleum Institute was 1,000 ppm.

In contrast, modern fuels are a complex mixture of blends derived from catalytic cracking, alkylation, catalytic reforming, polymerization, isomerization, and hydrocracking, plus small amounts of additives designed to improve the efficiency and reliability of the internal combustion engine. From 1925 to 1950, there was a gradual but steady increase in the compression ratio of the automotive engine intended to improve gasoline efficiency. This increase was more rapid during the 1950s, until it finally leveled off in the late 1960s.

The higher compression ratio made it necessary to increase the fuel octane rating by adding lead alkyls during petroleum refining. During the 1950s and 1960s, other changes also were made in automotive gasoline to aid performance. Additives were developed to minimize such problems as carburetor icing and fouling, valve and engine

deposits, spark plug fouling, fuel system corrosion, and poor fuel distribution. All of these factors have contributed to today's complex gasoline formulations.

In 1972, the compression ratio in U.S. passenger car engines was sharply lowered. This trend reversal created a car population with widely different octane requirements. To satisfy varied requirements while complying with regulations limiting lead antiknock additives, gasoline distributors marketed several grades of gasoline. This diversity in gasoline is diminishing, however, with the onset of low-lead gasoline cars.

Diesel Fuels

Diesel fuels are categorized as: diesel fuel oils for automobiles, city-buses and similar vehicles; fuels for diesel engines in trucks and tractors; fuels for railroad diesel engines; and heavy-distillate and residual fuels for large stationary and marine diesel engines.

They are characterized by their physical properties such as gravity, flash point, color, viscosity at 100°F (37.8°C), cloud point, pour point, sulfur content, aniline point, carbon residue based on 10 percent by weight, ash percentage by weight, octane index, octane number, and distillation temperature.

Fuel standards are based on physical parameters rather than chemical composition. Diesel fuel generally has a distillation range between 374°F (190°C) and 716°F (380°C) and a specific gravity (15°C/15°C) range between 0.76 and 0.935. The properties of diesel fuel overlap with those of kerosene, jet fuels, and burner fuel oils. Thus, all of these products are generally referred to as intermediate distillates.

Jet Fuels

Jet fuels closely resemble diesel fuels, although they have a lower flash point, indicating that they contain more low-molecular-weight compounds. Commercial kerosene was used as a fuel in early development work on jet aircraft in the U.S. It was chosen over gasoline because of its low volatility--a characteristic that would prevent vapor lock under certain flight conditions--and its availability as a commercial product with uniform characteristics. JP-1 was a military jet fuel developed during war time and it was followed by JP-2, JP-3, and JP-4. The latter is a blend of 25 to 35 percent kerosene and 65 to 75 percent gasoline components. JP-5 is a newly developed fuel for aircraft carriers. Commercial airline jet fuels are of different blends that fulfill a dual purpose in the aircraft:

providing energy and serving as a coolant for lubricating oils and other aircraft components. Jet fuel quality has improved over the years because of stringent end point specifications, and the addition of antioxidants, copper deactivators, corrosion inhibitors, anti-icing additives, and antistatic additives, as well as the inhibition of contaminants.

Residual Fuels

Grades 4, 5, and 6 are the designations given to the fuels most commonly used for space heating and/or process steam in commercial, industrial, and other large facilities. Typically, these fuels are used to provide steam and heat for industry. The largest single user of residual fuels is the electrical power generating industry, which consumes about 45 percent of available residual fuel.

Most advances in residual fuel technology since World War II have led to improvements in its use rather than in oil quality. The oil industry and boiler manufacturers have increased their efforts to desulfurize fuel oil and flue gas, and reduce fuel oil metal content. A number of additives have been developed that reduce residual fuel oil sludge, tube deposit formation, and corrosion, and that increase combustion efficiency.

Home Heating Fuels

Residential heating oil must be a clean product that does not form sediment in storage or leave much ash or other carbonaceous deposits upon burning. Because it may be stored outdoors during winter months, it must be fluid at low temperatures. The chemical composition of the product must be controlled to reduce smoke emissions.

The fuel oil most commonly used in homes is grade no. 2, which has a sulfur content of 2,500 ppm, far lower than the specified standard of 5,000 ppm. Nonexplosive at ordinary storage temperatures, it is an intermediate distillate, normally fractionated to a boiling range of 350°F to 650°F (177°C to 343°C). Grade no. 2 fuel oil contains paraffins (30.4 percent by weight), naphthenes (31.5 percent by weight), and aromatics (38.2 percent by weight), with benzene accounting for about 1/3rd of the aromatics.

Lubricating Oils

Lubricants are used to decrease friction and wear between two surfaces that move against each other. Such substances may be gaseous, liquid, semisolid or solid. Lubricants are also used to control temperatures, prevent corrosion and oxidation, provide electrical

insulation, avoid power losses through friction, and transmit power. Liquid lubricants, mineral oils, synthetic liquids, semisolid lubricants, and solid lubricants are generally oil based substances, and are known as lubricating oils.

A variety of compounds are added to lubricating oils to improve their physical or chemical properties. These additives are oxidation inhibitors that prevent the formation of acids and sludge, detergent and dispersants to control fuel soots and oil oxidation products, viscosity index additives to improve the viscosity properties of motor oils, corrosion inhibitors and antirust additives to coat metal surfaces, and pour point depressants to increase the fluidity of the oil at low temperatures.

Natural Gas

Natural gas is a combustible gaseous mixture of low-molecular-weight paraffin hydrocarbons generated or found in porous geologic formations below the surface of the earth. Its major constituent is methane and it contains some ethane along with small amounts of propane, butane, higher hydrocarbons, and sometimes nitrogen, carbon dioxide, hydrogen sulfide, and helium. Natural gas is mainly used by three types of customers: residential users with and without space heating or air conditioning, commercial establishments, and industrial complexes. Natural gas is a collective term used here for associated natural gas, dissolved natural gas, liquified natural gas, gas liquids, nonassociated gas, sour gas, sweet gas, and wet gas--products that are defined as:

- o Associated natural gas--free natural gas in immediate contact with but not in solution with crude oil in the reservoir.
- o Dissolved natural gas--natural gas in solution with crude oil in the reservoir.
- o Liquified natural gas (LNG)--natural gas cooled to -259°F (-162°C) so it forms a liquid at approximately atmospheric pressure. Natural gas in its liquid state must be regasified and introduced to the consumer at the same pressure as other natural gas. The cooling process does not alter the gas chemically and the regasified LNG is indistinguishable from other natural gases of the same composition. LNG is discussed in detail in the section of this report on liquified energy gases.
- o Natural gas liquids--liquid hydrocarbons that are gaseous at reservoir temperatures and pressures, but are recoverable by condensation or absorption.

- o Nonassociated natural gas--free natural gas in contact with, not dissolved in, crude oil in the reservoir.
- o Sour--gas found in its natural state, containing enough compounds of sulfur to make it impractical to use without purifying because of its corrosive effect on piping and equipment.
- o Sweet--gas found in its natural state, containing such a small amount of sulfur that it can be used without purifying with no deleterious effect on piping and equipment.
- o Wet natural gas--unprocessed or partially processed natural gas produced from strata containing condensable hydrocarbons.

Other Gases and Future Fuels

Currently, liquefied energy gases (imported LNG, LPG, and naphtha derived from crude oil) comprise about 3 percent of the energy consumed in the U.S. and are used to supplement domestic natural gas supplies. About 2 percent of the nation's energy is supplied by LPG, primarily propane. In 1976, 13 million customers, mostly in rural areas, used LPG as an energy source.

Traditional sources of methane will be supplemented in the future by new technologies. These will include pipeline quality gas from the gasification of coal and oil shale and methane derived from biomass.

With 1/2 the Btu content of gasoline, methanol, a fuel currently being combined with gasoline, releases 20 percent more energy through more efficient burning. It makes an automobile engine burn five times cleaner than with gasoline. Engine life is extended because alcohol burns cooler, and there is the added benefit of lower maintenance costs because of decreased hydrocarbon buildup, but aldehyde emissions may be increased. Compared with gasoline, methanol and ethanol offer a less expensive alternative for automobiles and small airplanes. Many different methanol combustion processes are currently being evaluated.

Converting engines to utilize alcohol fuels involves increasing the compression ratio to about 12 to 1, redesigning the fuel delivery system, changing the timing, installing a larger fuel tank that is not treated with turnplate, and changing gasket materials which may be adversely affected by alcohol (Fisher 1980).

National Fuel Consumption

Total U.S. fuel consumption over the last 30 years has more than doubled, rising from 32.96×10^{15} Btu's in 1948 to 78.01×10^{15} Btu's in 1978 (Council on Environmental Quality 1979). By the same token, petroleum use has increased from 11.81×10^{15} to 37.79×10^{15} Btu's, and natural gas consumption has risen from 4.90×10^{15} to 19.82×10^{15} Btu's. Use of coal remained at the level of 14×10^{15} Btu's over the same period. Figure 1 illustrates projected trends in oil and gas consumption through the year 2000.

U.S. oil and gas consumption in 1974 by various sectors is listed in Table 1. Households utilize oil and gas primarily for home heating and cooling, cooking, water heating, and clothes drying. Commercial uses include space heating and steam generation. Electric utilities use oil and gas in power plants to generate electricity which is, in turn, transmitted and distributed to the consumer. In the transportation sector, petroleum fuels are used in automobiles, aircraft, locomotives, ships, and tankers. Analysis of the table reveals that the ratio of natural gas to petroleum consumption is about 41 to 59. Analysis by sector suggests that transportation accounts for 32 percent; industrial, 27 percent; household and commercial, 25 percent; electric utilities, 12 percent; and the remaining 4 percent is consumed by raw materials and miscellaneous sectors (Loftness 1978). Per capita energy consumption in the U.S. for 1974 was 73.1×10^{15} Btu's, of which natural gas and petroleum accounted for 22.2×10^{15} Btu's and 30.9×10^{15} Btu's, respectively.

Fuel Consumption in Stationary Combustion

Utility boilers that produce steam to generate electricity consume 59 percent of the fossil fuel used in the U.S. Industrial boilers generating steam or hot water for process heat, electricity generation, or space heat use 24 percent; and boilers for space heating in commercial and institutional facilities consume 17 percent (U.S. Environmental Protection Agency 1979b). Some residential space heating takes place in boilers that are not represented in the percentages above. The fuels consumed in boilers in large quantities are natural gas, distillate oil, residual oil, and coal. In Table 2, the numbers of boilers are identified by the types of fuels used (U.S. Environmental Protection Agency 1979b).

Note: Reflects preliminary figures for 1975 and projections to the year 2000.

Source: Loftness 1978.

FIGURE 1
UNITED STATES OIL AND GAS CONSUMPTION FORECASTS

TABLE 1

1974 U.S. ENERGY CONSUMPTION
(10¹² Btu's)

Fuel	Household/ Commercial	Industrial	Electric Utilities	Transportation	Other ^a	Total
Natural gas	7,116	10,394	3,328	644	689	22,191
Petroleum						
Gasoline	---	---	---	12,596	---	12,596
Jet fuel	---	---	---	3,006	---	3,006
Distillate	3,000	769	396	2,027	50	6,242
Residual	1,125	1,182	3,018	685	62	6,072
Kerosene	289	83	---	---	---	372
Liquid gases	734	1,964	---	113	237	3,068
Other ^b	<u>1,241</u>	<u>391</u>	<u>---</u>	<u>160</u>	<u>1,307</u>	<u>3,099</u>
Total	13,505	14,783	6,742	19,231	2,345	56,646

Note: ---Represents zero or rounds to zero.

^aConstitutes raw materials and miscellaneous sectors.

^bIncludes naphthas, lubes and waxes, asphalt, petroleum coke, and miscellaneous.

Source: Adapted from Loftness 1978.

TABLE 2
NUMBER OF BOILERS BY FUEL TYPE

Type of Fuel	Number of Utility Boilers	Industrial/Commercial Boilers	Total Number of Boilers
Natural Gas	948	954,350	955,334
Distillate Oil	196	244,206	244,402
Residual Oil	1,038	389,104	390,142
Coal	<u>1,533</u>	<u>214,400</u>	<u>215,933</u>
Total	3,751	1,802,060	1,805,811

Natural gas is the primary fuel used in the industrial and commercial sectors. Industrial and commercial boilers consume more than half of the distillate and residual oil burned in boilers. This represents about 1/4th of the oil burned in the U.S. Most industrial and commercial facilities use cleaner-burning natural gas-fired boilers, which generate less pollution than coal- and oil-fired units.

Figure 2 illustrates the distribution of relative firing capacity by fuel type for each kind of boiler used by utilities, industry, and commercial facilities. Natural gas-fired boilers represent 45 percent of the total firing capacity in commerce and industry. Oil-fired boilers account for 31 percent, while coal units account for the remaining 18 percent of the firing capacity for industrial and commercial boilers. Of the utility boilers, natural-gas-fired boilers account for 26 percent; oil-fired, 31 percent; and coal-fired, 41 percent.

In residences, oil and natural gas are used for cooking, home heating, water heating, clothes drying, and space heating, as shown in Table 3. Residential gas utility customers in 1970 totaled 40,670,600, while commercial and industrial users totaled 3,392,000 and 193,800, respectively (American Gas Association 1974). The utility gas companies are the largest distributors of natural gas, followed by liquid fuel and bottled gas suppliers.

Source: (B) adapted from U.S. Environmental Protection Agency 1979a.

FIGURE 2
RELATIVE DISTRIBUTION OF TOTAL BOILER FIRING CAPACITY

TABLE 3

CONSUMPTION OF NATURAL GAS IN RESIDENTIAL END USES
(1970)

End Use	Type of Fuel	Number of Occupied Units (in thousands)		
		Urban	Rural	Total
Cooking	Utility gas	28,306.9	2,938.0	31,244.9
	Bottled gas	1,417.3	3,896.6	5,313.9
	Liquid fuel	192.4	110.5	302.9
House heating	Utility gas	30,909.1	4,104.8	35,013.9
	Bottled gas	919.8	2,887.4	3,807.2
	Liquid fuel	10,862.5	5,610.9	16,473.4
Water heating	Utility gas	31,656.0	3,303.4	34,959.4
	Bottled gas	962.0	2,182.7	3,144.7
	Liquid fuel	5,248.1	952.6	6,002.7
Clothes drying	Gas heated	6,780.4	1,059.3	7,839.7
Total occupied units in the U.S.		47,649.8	15,797.3	63,447.1

Source: American Gas Association 1975.

Fuel Consumption in Transportation

U.S. energy consumption in the transportation sector for 1973 was 18,763 trillion Btu's; the breakdown is shown in Table 4 below (Loftness 1978):

TABLE 4
ENERGY CONSUMPTION IN THE TRANSPORTATION SECTOR

Petroleum Products and Natural Gas Liquids	Trillion Btu's	Percent of Total
Gasoline	12,872	71.5
Jet fuel	2,131	11.3
Liquified gas	135	0.8
Distillate fuel oil	2,132	11.8
Residual fuel oil	731	4.1
Total	18,001	99.5

Note: Percentages may not add to 100 due to rounding.
Source: Loftness 1978.

Stationary Source Combustion

The rapid chemical combination of oxygen with the combustible element of a fuel is called "combustion." Three significant combustible elements are found in oil and natural gas: carbon, hydrogen, and sulfur. As a source of heat, sulfur is of minor importance, but it is of concern because of the corrosion and pollution problems associated with its presence.

The objective of good combustion is to release all exothermic heat while minimizing losses from combustion imperfections and superfluous air, as in the following generic equations:

These simple equations describe combustion in the variety of boilers and burners used to generate steam, heat, and electricity.

Boilers or boiler surfaces may be defined as those parts of tubes, drums, and shells that are part of the boiler circulatory system and are in contact with hot gases on one side and water or a mixture of water and steam on the other side. Boilers may be classified by heat transfer configuration, which is an important consideration in evaluating environmental impacts, partly because the configuration has a direct effect on combustion conditions (and resulting emissions). Boilers are classified as water-tube, fire-tube, and cast iron or shell type. Water-tube boilers are used in a variety of applications, ranging from supplying large amounts of process steam, to providing space heat for industrial and commercial facilities. Fire-tube boilers are not available with capacities as large as those of water-tube boilers, but they are used to supply process steam and space heating. Cast iron boilers are limited in size and are used only to supply space heat. The type of heat configuration by total boiler capacity is shown in Table 5 below (U.S. Environmental Protection Agency 1979b).

TABLE 5
BOILER TYPES AND CAPACITIES

Heat Transfer Configuration	Number of Boilers	Total Capacity (10 ⁶ Btu's/Hour)	Percent of Total Capacity	Use
Water-tube (utility)	3,751	3,647,500	45	Electricity generation
Water-tube (nonutility)	50,495	2,552,500	31	Process steam, electricity and space heat generation
Fire-tube	275,075	1,033,300	13	Process steam, space heat
Cast iron	<u>1,476,490</u>	<u>896,200</u>	11	Space heat
Total	1,805,811	8,129,500	100	

Water-Tube Boilers

In a water-tube boiler, hot combustion gases are in contact with the insides of tubes that are interconnected with common water channels and a steam outlet(s). Water-tube boilers generate high pressure and high-temperature steam. Used in a variety of utility, industrial, and commercial applications, they are available as packaged or field-erected units. Capacities of the packaged units range from 10,000 to 250,000 pounds of steam per hour. Higher capacity boiler units are field erected.

Water-tube boilers can efficiently burn any economically available fuel. They are sold in a variety of designs to fit any plant capacity and space requirement. Major types of water-tube boilers are vertical, vertically inclined, and horizontal. They are classified as units with: (1) natural circulation resulting from the difference between water and steam densities; or (2) forced circulation achieved with pumps that circulate water and steam through the boiler. Forced circulation boilers can operate in a supercritical range at capacities exceeding 10 million pounds of steam per hour. (Figure 3 compares a water-tube boiler with a fire-tube boiler, discussed below.)

Fire-Tube Boilers

In fire-tube boilers, combustion products flow through a tube that is surrounded by a water basin (Figure 3). These units are used primarily for heating, generating industrial process steam, and as portable power boilers where loads are relatively constant because they are susceptible to structural failure when subjected to large variations in steam demand. These units produce steam more efficiently than a simple shell or cast iron boiler because the water basin absorbs heat through the shell and also through the tubes.

Most fire-tube boilers have internal furnaces, i.e., the combustion chamber is enclosed in the boiler shell, unlike an external arrangement in which the boiler shell and combustion chamber are separate. Internal furnaces are preferred because of better water circulation and easier ash removal. There are six types of fire-tube boilers: horizontal return tubular, scotch marine, vertical, locomotive, short fire-box, and compact boilers.

Cast Iron Boilers

Cast iron or shell boilers are used in homes and small commercial operations to produce low-pressure steam or hot water. A residential cast iron boiler is a small, round unit in which the furnace is surrounded by a water basin. Flues allow combustion products to

A WATER-TUBE BOILER

A FIRE-TUBE BOILER

Source: Adapted from U.S. Environmental Protection Agency 1979a.

**FIGURE 3
SIMPLIFIED DIAGRAMS OF BOILERS**

escape from the combustion chamber and transfer heat from the gases to the water. Cast iron boilers are reliable, with an average life of about 50 years. They require little maintenance and can handle overloading or demand surges. The major problem associated with cast iron boilers is that the sections tend to deform, which may cause flue gases to leak from the joints.

Oil Burner

The oil burner converts fuel oil from a liquid phase into a combustible mixture. A number of different kinds of oil burners are in residential use, including sleeve burners, natural-draft pot burners, and air-atomizing and pressure-atomizing gun burners. The most common and modern type is the pressure-atomizing burner, shown in Figure 4, which accounts for 80 percent of the oil burners used to heat homes in the U.S.

The important feature of a high-pressure atomizing gun burner is its method of air delivery. It completely burns oil with the smallest quantity of air by properly proportioning and mixing the atomized oil and air required for combustion. The essential working parts of the burner are the electric motor, squirrel-cage-type blower, housing, fuel pump, electric ignition, and a primary control. Fuel oil is pumped from the tank through the pump gears, and oil pressure is regulated by an internal valve at a pressure of 100 to 300 psi at the burner nozzle. The oil is then ignited, atomized, and burned.

Safety is an important consideration with oil burners and one of the most important safety features on an automatic oil burner is the primary control. This will shut off the burner when it is not functioning properly, protecting against such occurrences as incorrect primary air adjustments, dirt in the atomizing nozzle, inadequate oil supply, and improper combustion.

Gas Burner

The gas burner converts natural gas into a heat source that is used in residential heating and cooling systems. Most residential units are warm, forced-air furnaces with capacities of up to about 300,000 Btu's per hour. In residential gas heaters, air discharge and return is accomplished in one of two ways: by gravity or by a pressure blower. The furnace is enclosed in a rectangular steel casing and gas is burned in a primary combustion space within a metal-walled heat exchanger.

Natural gas, which is supplied by utility companies through pipelines, is the most widely used home heating fuel in the U.S. In the home, low-pressure gas is burned in approved gas burners that

Source: The MITRE Corporation 1977.

FIGURE 4
A HIGH-EFFICIENCY OIL BURNER

have an essentially trouble-free design and adequate safety controls. Natural gas generally burns efficiently; however, its flammable characteristics are somewhat more dangerous than those of fuel oil. Figure 5 shows a forced-circulation, warm-air heating system used for residential oil- and gas-fired furnaces.

Mobile Source Combustion

The term mobile combustion refers to the combustion of petroleum-derived fuels to produce heat energy, which in turn is converted into mechanical energy that can drive a piston, rotor, or turbine in an internal combustion engine. The automobile engine's basic function is to transform the chemical energy of an air-fuel mixture into the mechanical energy required to propel a vehicle. Quite simply, the burning of fuel inside the engine produces mechanical energy in the form of a rotating shaft. This working energy is transmitted to the wheels of a vehicle by a power-transmission system.

Gasoline Engine

Automobile engines are driven by reciprocating internal combustion gasoline engines that operate on the four-cycle principle developed by Nikolaus Otto in 1876. Present four-, six-, and eight-cylinder engines are four-cycle, gasoline-burning piston engines, as shown in Figure 6.

A basic component of the internal combustion engine is the cylinder, closed at one end, in which a piston is free to move up and down. When a mixture of air and gasoline is burned above a piston, the resulting expansion drives the piston down into the cylinder. This vertical thrust is transmitted by a connecting rod and bearings to an offset crankshaft, where it is converted into rotary motion. In a gasoline engine, fuel and air are mixed before they enter the combustion chamber and then are spark-ignited. In the four-cycle engine illustrated in Figure 6, each piston travels alternately from the top to the bottom of the cylinder four times as it completes the following cycle:

- o Intake stroke. Piston moves down, pulling a mixture of air and gasoline into the cylinder through the open intake valve.
- o Compression stroke. Intake valve closes, piston moves up and compresses the mixture.
- o Power (expansion) stroke. Near the top of the compression stroke, the highly compressed mixture of air and gasoline is ignited by the spark plug. Expanding rapidly, it forces the piston back down to the bottom of the cylinder.

Source: Adapted from McGraw Hill 1977.

FIGURE 5
FORCED AIR SYSTEM FOR RESIDENTIAL OIL AND GAS FURNACES

A. The 4-stroke cycle. Fuel is drawn into the cylinder from the carburetor (intake stroke), compressed by the rising piston (compression stroke), and ignited by the spark plug; piston is forced downward (power stroke) by burning gasoline; burned gases are expelled (exhaust stroke).

B. The Automobile Fuel System. The fuel pump moves gasoline from the tank to the carburetor, discussed below.

Source: Adapted from McGraw Hill 1977.

FIGURE 6
THE AUTOMOBILE'S FOUR-STROKE CYCLE AND FUEL SYSTEM

- o Exhaust stroke. Exhaust valve opens; the piston moves up and sweeps the cylinder clear of burned gases. At the end of the exhaust stroke, the piston is at the top of the cylinder with the exhaust valve closing, ready to begin the cycle again.

The valve mechanism plays an important role from the standpoint of pollution. One intake and one exhaust valve are provided for each cylinder. Valves have three distinct functions: (1) the intake valve admits an air-gasoline mixture in the carburetor and intake manifold, (2) the intake and exhaust valves seal off the cylinder space during compression, and (3) the exhaust valve opens to discharge exhaust gases from the engine. Combustion-chamber temperatures range from 50° to 5,000°F (65.5° to 2,760°C) and heat generated during combustion is not fully transformed into useful energy. The unused heat is generally dissipated by circulating water through jacketed spaces in the cylinder head and cylinder block.

The fuel system of an automobile engine, also illustrated in Figure 6, consists of a fuel tank, remote reading fuel gauge, filter, fuel pump, and carburetor. The fuel pump usually is of the diaphragm type. The carburetor, shown in Figure 7, meters and atomizes the fuel so air and gasoline are mixed in a ratio of about 14.7 to 1. Modern engines continuously vary this ratio for maximum operating efficiency. The gasoline and air mixture formed by the carburetor is carried to each cylinder by a ducting system called the intake manifold. Exhaust gases travel from the exhaust ports of the engine through a manifold connected to the exhaust pipe and the muffler. Mufflers are cylindrical or oval chambers of sheet steel installed between the exhaust pipe and tailpipe. The environment of the muffler is highly corrosive and coatings of zinc, aluminum, or ceramic are often used to extend muffler life.

The compression ratio expresses the relationship of the cylinder volume when the piston is at the bottom of its stroke to the volume when the piston is at the top of its stroke. Fuel burns more efficiently at higher compression ratios. For example, with a compression ratio of 6 to 1, only 25 percent of potential fuel energy is converted into mechanical power by the engine; however, with a compression ratio of 12 to 1, the efficiency is close to 32 percent. Compression ratios in American automobiles generally vary from 8 to 1 to more than 11 to 1.

Diesel Engine

The diesel engine differs from other internal combustion engines mainly in the way fuel is introduced and ignited. The diesel engine is more heavily built than a gasoline engine, and has fewer moving parts. Fuel is sprayed directly into the combustion chamber and

In the automobile carburetor, measured amounts of fuel are mixed with air and sprayed through the intake manifold to the cylinders. After ignition, burnt gases are forced out by the pistons through the exhaust manifold, exhaust pipe, muffler, and tailpipe, and then into the atmosphere.

Source: Adapted from McGraw Hill 1977.

FIGURE 7
THE CARBURETOR

ignited by the high temperature to which air in the combustion chamber has been heated during the compression process. The engine operates on a thermodynamic cycle in which the air pressure is high enough to ignite the fuel subsequently injected into the combustion chamber. The diesel engine utilizes a wide variety of fuels with higher thermal efficiency than its gasoline counterpart, and it has consequent economic advantages under many service applications.

The diesel engine cycle consists of air compression in the combustion chamber, fuel injection into the combustion chamber, combustion and expansion of the hot gases, and exhaust. The cycle then begins again and the process continues. Combustion is considered to take place at a constant pressure. The method of fuel introduction is the key element in the efficient operation of a diesel engine. A high pressure pump is used to inject fuel at precisely the proper moment in the stroke, which is accurately metered.

Because of its use of heavy fuels and its combustion system, the diesel engine has certain limitations. Smoking occurs in the exhaust if an attempt is made to use more than 60 to 70 percent of the air in the cylinder during combustion. This smoking determines the maximum power produced by the engine. The air in diesel engines is compressed until its pressure is over 500 psi and its temperature around 800°F (427°C).

Modern diesel engines used in trucks, buses, and tractors range from a single-cylinder model with a bore and stroke of little more than three inches, and a weight of 200 pounds, that produces 7 horsepower at 2,400 revolutions per minute; to a version with 16 cylinders, a bore of nine inches, a stroke of 10.5 inches, and a weight of 41,000 pounds, that produces 3,600 horsepower at 1,100 revolutions per minute.

Stationary Source Emissions

Burning oil and natural gas causes emissions of nitrogen oxides (NO_x) and relatively minor amounts of particulate matter, sulfur dioxide (SO_2), carbon monoxide (CO), and hydrocarbons (HC), with the quantity of pollutants dependent on the extent of combustion. The following paragraphs discuss atmospheric emissions from oil- and gas-fired boilers that produce electricity, steam, and heat.

Particulate Emissions

Fuel oil properties such as API gravity, carbon residue, ash content, viscosity, and volatility are important in determining particulate emissions from oil-fired units. These properties influence atomization and vaporization, which contribute to proper combustion.

Proper atomization is necessary to achieve complete, smoke-free oil combustion. The quantity of emitted particulates is directly dependent on the size of the oil droplets, which is a function of burner type or atomization method. Incomplete vaporization of larger oil droplets contributes to particulate emissions.

Fly ash particles emitted from oil-fired power plants are crystallites--principally magnesium, sulfur, and vanadium. The metals present in fuel oils are concentrated in the ash products that remain after combustion. For example, a fuel oil containing 50 to 400 ppm of vanadium could result in a fly ash content of 5 to 40 percent vanadium. Oil- and coal-fired boilers produce fly ash containing several water soluble chemicals, including carbon, H_2SO_4 , NH_4HSO_4 , MgO , $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, V_2O_5 , $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$, Fe_2O_3 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, NiO , NiSO_4 , Al_2O_3 , $\text{Al}_2(\text{SO}_4)_3$, SiO_2 , Na_2SO_4 , K_2SO_4 , CaO , and CaSO_4 (Henry and Knapp 1980).

Uncontrolled particulate emissions from firing no. 6 residual oil depend on the oil's sulfur content. The sulfur level affects SO_3 adsorption, thus, greater particulate formation occurs with oils of higher sulfur content. Particulate emissions from residual oil firing decrease as the boiler size increases, probably because of better combustion control and increased maintenance. With distillate oil, particulate emissions depend on the design of the boiler barrier rather than the size of the boiler (Offen et al. 1976).

Operating parameters affecting particulate emissions are boiler load, cycling, and maintenance. At low boiler load conditions, particulate matter may be lowered by 30 to 40 percent with utility and by as much as 60 percent with small industrial and commercial units firing grade 6 oil. No significant particulate reduction has been noted at low loads from boilers firing any of the lighter grades. If loading is too low, proper combustion conditions cannot be maintained and particulate emissions may increase drastically. Any condition that prevents proper boiler operation can result in excessive particulate formation.

Gas-fired boilers do not generate large particulate emissions of coke or soot which result from incomplete combustion (Cato et al. 1974). Emission factors for uncontrolled particulates from oil- and gas-fired boilers are listed in Tables 6 and 7.

Sulfur Oxides Emissions

The predominant sulfur oxide (SO_x) is sulfur dioxide (SO_2), although sulfur trioxide (SO_3) can also be emitted. These emissions are often reported collectively as SO_x , even though SO_3 may constitute only 1 to 3 percent of the total (U.S. Environmental

TABLE 6

EMISSION FACTORS FOR FUEL OIL COMBUSTION

Pollutant	Utility		Industrial and Commercial Boilers				Residential	
	Residual Oil Boilers		Residual Oil		Distillate Oil		Distillate Oil Boilers	
	lb/10 ³ gal	kg/10 ³ liter	lb/10 ³ gal	kg/10 ³ liter	lb/10 ³ gal	kg/10 ³ liter	lb/10 ³ gal	kg/10 ³ liter
Particulates	10(S)+3 ^a 10 ^b 7 ^c	1.25(S)+0.38 ^a 1.25 ^b 0.88 ^c	10(S)+3 ^a 10 ^b 7 ^c	1.25(S)+0.38 1.25 ^b 0.88 ^c	2	0.25	2.5	0.31
Sulfur dioxide	157S	19S	157S	19S	142S	17S	142S	17S
Sulfur trioxide ^d	2S	0.25S	2S	0.25S	2S	0.25S	2S	0.25S
Nitrogen oxides	15C ^e (50) ^f	12.6(6.25)	60	7.5	22	2.8	18	2.3
Carbon monoxide	5	0.63	5	0.63	5	0.63	5	0.63
Hydrocarbons	1	0.12	1	0.12	1	0.12	1	0.12

^aParticulate values for grade 6 oil where S is the percentage by weight of sulfur in the oil.

^bParticulate values for grade 5 oil.

^cParticulate values for grade 4 oil.

^dS is the percentage by weight of sulfur in the oil.

^eAll boilers except tangentially fired boilers.

^fFor tangentially fired boilers.

Source: U.S. Environmental Protection Agency 1977d.

TABLE 7

EMISSION FACTORS FOR NATURAL GAS COMBUSTION

Pollutant	Utility Boilers		Industrial Process Boilers		Residential and Commercial Heaters	
	(lb/10 ⁶ ft ³)	(kg/10 ⁶ m ³)	(lb/10 ⁶ m ³)	(kg/10 ⁶ m ³)	(lb/10 ⁶ ft ³)	(kg/10 ⁶ m ³)
Particulates	15	240	18	290	19	302
Sulfur oxides ^a	0.6	9.6	0.6	9.6	0.6	9.6
Nitrogen oxides	600	9,600	120-230 ^b	1,920-3,700 ^b	80-120 ^c	1,280-1,920 ^c
Carbon monoxide	17	270	17	270	20	320
Hydrocarbon	1	16	3	48	8	128

^aBased on average sulfur content of natural gas of 2,000 grains/10⁶ft³ (4,600 g/10⁶m³).

^b120 (1,920) for smaller industrial boilers and 230 (3,700) for large industrial boilers.

^c80 (1,280) for domestic heating units and 120 (1,920) for commercial units.

Source: U.S. Environmental Protection Agency 1977d.

Protection Agency 1977d). SO_x emissions depend on the sulfur content of the fuel oil and are not affected by boiler size, burner design, or grade of fuel. Table 6 presents uncontrolled SO_x emission factors for firing residual and distillate oil in various boiler types.

The natural gas used in boilers has chemical additives that detect sulfur leaks. Small amounts of SO_x are emitted from natural gas-fired units, as indicated by the SO_x emission factors listed in Table 7.

Sulfate emissions also are of concern in boiler operations. Sulfur-bearing residual oil produces sulfates directly in combustion (primary) or when sulfur dioxide emissions are converted to sulfates in the atmosphere (secondary). Not much is known about formation mechanisms or the relative contributions of various sources of sulfates, but it is believed that sulfates represent a significant environmental problem. Epidemiological studies have implicated suspended water soluble sulfates as respiratory irritants. Primary sulfates represent 3 to 12 percent of the sulfur oxides discharged from oil combustion in boilers. Primary sulfates can have a direct impact on people, particularly when they are emitted from low-level stacks in urban areas. Secondary sulfates are the dominant source of "remote pollution," which manifests itself as acid rain or by impairing visibility. The potential impact of sulfates from boilers can vary significantly with the type of boiler, mode of operation, and fuel composition.

Sulfate emissions from oil-burning sources are 3 to 10 times greater than from sources burning coal with an equivalent sulfur content. It is believed that the higher flame temperatures, the vanadium and nickel content, and the lack of particulate control devices for oil-fired units contribute to observed sulfate emissions (Homolya and Cheney 1978).

Much of the combustion in industrial and commercial boilers is likely to be poorly controlled for conditions such as excess air. If the industrial and commercial sectors continue to burn large amounts of oil, more effective control of both large and small oil-fired boilers would be necessary to effectively reduce exposure of the U.S. population to sulfates.

Nitrogen Oxides Emissions

Nitrogen oxides are produced during fuel oil combustion by two mechanisms, namely, oxidation of fuel-bound nitrogen and thermal fixation of nitrogen present in combustion air. The quantity of fuel NO_x emitted depends on the nitrogen content of the fuel and the

amount of oxygen available. The quantity of thermal NO_x , on the other hand, is largely a function of peak flame temperature and the amount of oxygen. It also depends on boiler size, firing configuration, and operating practices. Nitrogen oxides are mainly nitric oxides (NO) and nitrogen dioxide (NO_2). NO usually makes up more than 90 percent of NO_x when the pollutant is initially emitted from a boiler. In the atmosphere, most NO eventually becomes NO_2 .

Residual oil-fired boilers contribute a major portion of total airborne NO_x emissions, while distillate oil-fired and natural gas-fired boilers contribute a minor amount. These emissions depend upon parameters such as combustion air temperature, flue gas recirculation heat release rate, excess air, and the air-to-fuel ratio. The effects of these parameters are fairly consistent with all types of boilers and fuels. Heating combustion air increases flame temperature and enhances formation of thermal NO_x . Excess air seems to encourage thermal NO_x generation.

The quantity of nitrogen oxides emitted from natural gas-fired boilers is a function of the temperature in the combustion chamber and the cooling rate of the combustion products. These values vary considerably with the type and size of unit. (Factors for uncontrolled NO_x emissions from oil- and gas-fired boilers are provided above in Tables 6 and 7, respectively.)

Carbon Monoxide Emissions

The rate of carbon monoxide (CO) emissions from boilers is heavily dependent upon the efficiency of fuel combustion. (Again, factors for uncontrolled carbon monoxide emissions from oil- and gas-fired boilers are provided above in Tables 6 and 7, respectively.) Efficiency of combustion and, consequently, boiler maintenance have a major influence on CO emissions. Because proper combustion lowers emissions, the units should be operated while carefully controlling excess air, using high combustion temperatures, and providing for intimate air-fuel contact. Improper operation and on/off cycling of smaller boilers can increase CO emissions by several orders of magnitude. This is most likely to be the case with small, frequently unattended units, and not with larger units that are continuously operated and routinely maintained.

Hydrocarbon Emissions

The rate of hydrocarbon (HC) emissions from boilers is also dependent upon fuel combustion efficiency. Hydrocarbon emissions are minimal when proper combustion practices are used. (Again, factors for uncontrolled hydrocarbon emissions from oil- and gas-fired boilers are listed in Tables 6 and 7, respectively.) Combustion

efficiency is related to the condition of the boiler. As with CO, careful control of excess air, use of high combustion temperatures, and provision of intimate fuel-air contact will minimize HC emissions. Hydrocarbon emissions from oil- and gas-fired units generally are negligible unless the units are improperly operated or maintained. Then emissions may increase by several orders of magnitude.

Hydrocarbons include volatile organic compounds (VOC), such as methane, formaldehyde, ethane, ethylene, acetylene, acetone, propane, propylene, n-butane, isobutane, n-pentane, hexane, heptane, octane, cyclohexane, benzene, and toluene. Stationary combustion sources using residual, distillate, or natural oil emit an estimated 5 percent of evaporative VOC emissions which total 28.3×10^6 million tons per year (U.S. Environmental Protection Agency 1978b).

Another group of hydrocarbons, polycyclic organic matter (POM) has been defined most simply as all organic matter with two or more benzene rings. This class of compounds has been considered hazardous, but little is known about the relative amounts of POM discharged by various sources.

Two interrelated boiler characteristics affect the amount of POM generated: the type of fuel used and combustion efficiency. In general, more POM would be expected from burning oil than from gas. Larger boilers operated continuously under well-controlled, well-maintained conditions would produce less POM. More common small boilers, which generally are loosely controlled and poorly maintained, can emit much larger quantities of POM per unit of fuel burned.

The POM class includes polynuclear aromatic hydrocarbons commonly identified as PAHs, and nitrogen-containing heterocyclic compounds. Although the physical states of POM and soot are different, they probably have common origins and similar chemical reactivity. The materials labeled POM are emitted in small or trace quantities during the combustion of residual oil. Studies of the mode of formation and destruction of POM in the combustion process are difficult to carry out because of the low concentrations, the lack of simple analytical procedures for identifying them, and the large number of individual compounds making up this class of material. Typical POMs that have been observed are anthracene, pyrene, methyl anthracene, fluoranthene, methyl fluoranthene/pyrene, chrysene, perylene, benzo(ghi)perylene, and coronene (U.S. Environmental Protection Agency 1978a).

The relationship between fuel type, boiler efficiency and efficiency of one POM, benzo(a)pyrene (BaP), is illustrated in Table 8 (Hangebrauck et al. 1967).

TABLE 8

RELATIVE BENZO(A)PYRENE EMISSION RATES FROM STATIONARY
FUEL COMBUSTION SOURCES

Fuel	Estimated Emission Rate (ug/10 ⁶ Btu's)
Coal	1,451,790
Oil	200
Gas	100

These data are average values for gas and oil furnaces and suggest that oil- and gas-fired furnaces produce less BaP than coal-fired furnaces. A recent study by the U.S. Environmental Protection Agency (EPA), which assessed pollution from fossil fuel combustion boilers, suggests that the fuel burned in utility boilers would produce less POM than similar fuels burned in industrial and commercial boilers (U.S. Environmental Protection Agency 1979b). Small, oil-burning industrial and commercial boilers are located mostly in urban areas and emit POM at low elevations from many sources. These sources could have a greater impact on human health than larger, more remote sources.

Estimated controlled emissions of criteria pollutants from utility, industrial, and commercial boilers for 1975 are shown in Table 9, along with EPA estimates for total annual emissions for the U.S. (U.S. Environmental Protection Agency 1979b).

TABLE 9
ESTIMATED EMISSIONS OF FIVE
CRITERIA POLLUTANTS FROM BOILERS
(10⁶ tons/year)

Sector/Fuel	Particulate	SO _x	NO _x	CO	HC
<u>Utility</u>					
Oil	0.08	1.49	1.11	Unknown	Unknown
Gas	<u>0.00</u>	<u>0.00</u>	<u>1.0</u>	Unknown	Unknown
Total	0.08	1.49	2.11	0.27	0.09
<u>Industrial/Commercial</u>					
Oil	0.11	1.55	0.44	Unknown	Unknown
Gas	<u>0.05</u>	<u>0.00</u>	<u>0.43</u>	Unknown	Unknown
Total	0.16	1.55	0.87	0.21	0.07
Total U.S. Emissions ^a	16.0 ^a	28.5 ^a	24.4 ^a	95.0 ^b	28.9 ^b

^aSource: U.S. Environmental Protection Agency 1976, based on NEDS data.

^bSource: U.S. Environmental Protection Agency 1979b.

The particulate emission values reflect an assumed 95 percent average efficiency for 1975. The data indicate that oil- and gas-fired boilers contribute 1.5 percent of the particulates emitted during combustion in the U.S., 10.7 percent of the SO_x, 12.2 percent of the NO_x, 0.22 percent of the CO, and 0.24 percent of the hydrocarbons.

Trace Metals

Many of the trace metal ions present in oil (e.g., arsenic, cadmium, and mercury) have the potential for being emitted as toxic substances, while vanadium and nickel have the potential for

catalyzing undesirable atmospheric transformations such as the conversion of sulfur dioxide to sulfates. The sparse data available on trace elements suggest that their presence and concentrations in crude oils vary. Refining concentrates trace metals in oil by a factor of 5 to 10 or more. Hence, potentially hazardous trace metal compounds may be discharged in the combustion of refined oil in small boilers.

An EPA study shows that actual residual oil composition may vary (U.S. Environmental Protection Agency 1978b). Of the 60 or so detectable trace species in residual oil, vanadium concentrations were found as low as 10 ppm by weight and as high as 300 ppm by weight. This wide variation is due to the variation in imported crude oils and the common refinery practice of blending the bottoms from several different crudes into one final residual oil. Table 10 illustrates an average residual oil composite analysis (U.S. Environmental Protection Agency 1978b).

Of the most abundant trace metal compounds formed, only silicon dioxide (SiO_2) and vanadium pentoxide (V_2O_5) remain constant over the temperature range between 440°F and 2,780°F. Aluminum, iron, and magnesium tend to form oxides at 980°F and above and sulfates at 710°F and below. Nickel and calcium predominantly form oxides at 2,780°F, but form mostly sulfates at lower temperatures. The predominant sodium compound at 2,780°F is sodium silicate (Na_2SiO_3), but, below that temperature, sodium tends to favor sulfates. The metal sulfate distribution agrees well with the SO_2 distribution, which is highest at higher temperatures where there are fewer metal sulfates, and lowest at lower temperatures where there are more metal sulfates. The sulfur from residual oil reacts to form predominantly SO_2 at 2,780°F, but as the combustion temperature decreases, more of the sulfur is taken up in metal sulfates. Lead emissions from all oil combustion sources were estimated to be 110 tons in 1975 (U.S. Environmental Protection Agency 1977c). These lead emissions are comparatively small and of little concern.

Indoor Emissions

The combustion of oil and natural gas for cooking, space heating, etc., in the residential sector causes the indoor generation of air pollutants, namely nitrogen dioxide (NO_2), nitric oxide (NO), carbon dioxide, sulfur dioxide, carbon monoxide, and hydrocarbons. Indoor air quality is a complex function of outdoor pollutant concentrations, building permeability, meteorological conditions, ventilation system design, and indoor generation of pollutants.

TABLE 10
AVERAGE RESIDUAL OIL COMPOSITE ANALYSIS

Element	Concentration ^a	Element	Concentration ^a
Carbon	85.1%	Uranium	0.7 ppm
Hydrogen	11.2%	Antimony	0.4 ppm
Sulfur	2.5%	Doron	0.41 ppm
Nitrogen	4,400.0 ppm	Gallium	0.4 ppm
Vanadium	160.0 ppm	Indium	0.3 ppm
Nickel	42.2 ppm	Silver	0.3 ppm
Potassium	34.0 ppm	Germanium	0.2 ppm
Sodium	31.0 ppm	Tahllium	0.2 ppm
Iron	18.0 ppm	Zirconium	0.2 ppm
Silicon	17.5 ppm	Strontium	0.15 ppm
Calcium	14.0 ppm	Bromine	0.13 ppm
Magnesium	13.0 ppm	Fluorine	0.12 ppm
Chlorine	12.0 ppm	Ruthenium	0.1 ppm
Tin	6.2 ppm	Tellurium	0.1 ppm
Aluminum	3.8 ppm	Cesium	0.09 ppm
Lead	3.5 ppm	Beryllium	0.08 ppm
Copper	2.8 ppm	Iodine	0.06 ppm
Cadmium	2.27 ppm	Lithium	0.06 ppm
Cobalt	2.21 ppm	Mercury	0.04 ppm
Rubidium	2.0 ppm	Tantalum	0.04 ppm
Titanium	1.8 ppm	Thodium	0.03 ppm
Manganese	1.33 ppm	Gold	0.02 ppm
Chromium	1.3 ppm	Platinum	0.02 ppm
Barium	1.26 ppm	Scandium	0.02 ppm
Zinc	1.26 ppm	Bismuth	0.01 ppm
Phosphorus	1.1 ppm	Cerium	0.006 ppm
Molybdenum	0.9 ppm	Tungsten	0.004 ppm
Arsenic	0.8 ppm	Hafnium	0.003 ppm
Selenium	0.7 ppm	Yttrium	0.002 ppm
		Niobium	0.001 ppm

^aConcentration by weight.

Source: U.S. Environmental Protection Agency 1978.

Many indoor-generated pollutants are emitted in a fugitive manner, i.e., they enter the indoor atmosphere through uncontrolled stove and oven emissions and from leaks from faulty combustion systems such as space heaters, gas-fired hot water heaters, and gas dryers. Energy conservation measures in single family homes and apartment buildings tend to aggravate this problem by concentrating indoor pollutants.

Emissions from Gas Stoves and Ovens

Unvented gas stoves can contribute measurable quantities of carbon monoxide to the indoor atmosphere (Yocum et al. 1971). Indoor air quality is degraded by combustion products from gas stoves, especially NO_2 , NO, and CO emissions. Pilot lights on gas stoves generate measurable amounts of NO, NO_2 , and CO when a stove is not in use. Highest indoor concentrations of stove-generated pollutants occur in the winter when houses are tightly closed. The amounts of pollutants generated are directly related to the number of burners in operation and the amount of gas consumed. Vented stove hoods are moderately effective in removing gaseous pollutants, but recirculating hoods are not. Stove use and outdoor air quality influence indoor air quality. This joint influence is a function of house permeability. Concentrations of pollutants in the kitchen are always higher than in other parts of the house (Cote et al. 1974).

Emissions of Sulfur Dioxide and Sulfates. The literature indicates that indoor SO_2 concentrations are primarily the result of the introduction of outdoor-generated SO_2 into buildings. Few studies demonstrate indoor SO_2 generation from oil-burning heating systems (Yocum et al. 1974) or gas stoves (Hollowell et al. 1976). It is suggested that SO_2 is reactive and may be differentially absorbed by interior walls, ceilings, floors, and their interior surfaces and finishes. Differences in room sizes, building materials, fixtures, furniture, ventilation rates, and occupancy are probable variables that account for differences in indoor-to-outdoor ratios (Anderson 1972).

A study conducted in Boston and Cambridge homes (Arthur D. Little 1975) lends support to the results cited above. In a study conducted on 60 homes heated with oil, coal, or gas in Rotterdam, the Netherlands, investigators concluded that indoor SO_2 concentrations are not significantly affected by the heating system used if it is in good condition, but they reported that indoor concentrations of SO_2 were 3.8 times the outdoor levels for a 30-year-old home where a heater was believed to be faulty (Biersteker et al. 1965). They noted that newer homes tend to have lower SO_2 emissions than older homes.

Recently, pilot measurements of SO₂ and pollutants were taken at various indoor and outdoor locations by a team of investigators from the Lawrence Berkeley Laboratory of the University of California (Hollowell et al. 1976). SO₂ levels observed by this group with a gas oven operating at 550°F (287°C) for approximately 20 minutes ranged from <15 to 110 ug/m³, with average values varying:

<u>Stove Condition</u>	<u>SO₂ (ug/m³)</u>
Kitchen background	<15-40
One burner on, no grate	25-65
One burner on with grate	<15-90
One burner on with grate and all stainless steel pans	<15-80

A study conducted in Germany on air pollution due to home heating systems suggests that the systems are responsible for 58.5 percent of indoor SO₂ emissions that total 5,092 tons per year (Gredischnik 1972).

Nitrogen Oxides and Nitrates. Nitrogen oxides concentrations are reported to be lower outdoors than at all locations indoors because of the gas stove, an indoor nitrogen oxide source (Cote et al. 1974). An investigation of indoor and outdoor nitrogen oxides concentrations suggests that indoor peaks seem to be related to rush hour traffic. The impact of gas stoves on indoor NO_x concentrations was studied extensively (Cote et al. 1974). Table 11 illustrates the results of the laboratory study, which concluded the following:

- o The gas stoves tested emit significant quantities of nitrogen oxides in the following ranges depending upon stove operation: NO, 90 to 130 ug per Kcal, 200 to 1,000 mg per hour; NO₂, 50 to 80 ug per Kcal, 100 to 500 mg per hour.
- o Pollutant emissions from the newer stove were not consistently higher or lower than those from the older stove for the range of operations evaluated.
- o The different designs of the burners of the two stoves did not appear to have consistent and reproducible effects upon pollutant emissions. Tests designed to evaluate the effect of air-fuel mixture upon burner operation indicated that the

TABLE 11

POLLUTANT EMISSIONS FROM GAS APPLIANCES^a

Appliance	Operation	Heat Input Rate (Kcal/hr)	Pollutant Emission Factors (µg/Kcal)			Pollutant Emission Rates (mg/hr)		
			NO	NO ₂	CO	NO	NO ₂	CO
Older gas stove with cast iron burners	Pilot lights	150	45.3	54.6	419	6.8	8.2	62.9
	1 burner, high flame	2,700	92.6	51.8	382	250.0	140.0	1,031.0
	3 burners, high flame	6,780	117.0	72.8	475	793.0	494.0	3,220.0
	Oven							
	Transient	2,300	157.0	159.0	1,790	361.0	366.0	4,117.0
	Steady-state	2,200	91.4	73.1	530	201.0	161.0	1,166.0
	Broiler							
	Transient	3,000	137.0	123.0	1,350	411.0	369.0	4,050.0
	Steady-state	3,800	88.8	48.5	818	337.0	184.0	3,108.0
New gas stove with pressed steel burners	Pilot lights	100	4.7	18.6	842	0.5	1.9	84.2
	1 burner, high flame	3,500	130.0	79.0	510	455.0	277.0	1,785.0
	3 burners, high flame	10,200	138.0	65.6	315	1,408.0	669.0	3,213.0
	Oven							
	Transient	4,000	331.0	79.0	1,010	1,324.0	316.0	4,040.0
	Steady-state	2,200	77.9	50.4	1,620	171.0	111.0	3,564.0
	Broiler							
	Transient	4,900	126.0	80.6	846	617.0	395.0	4,145.0
	Steady-state	3,700	136.0	57.1	757	503.0	211.0	2,800.0
Unvented space heater	Low flame, steady-state	2,800	76.4	46.4	632	214.0	130.0	1,770.0
	High flame, steady-state	6,200	135.0	43.8	319	837.0	272.0	1,978.0
Domestic gas furnace	- - -	Approx 30,000		90.0	36	2,700.0	1,080.0	

^aSummary for several typical operating dwellings in Hartford, Connecticut.

Source: Cote et al. 1974

best blue luminous flame was produced at an intermediate air shutter opening for each stove. Variation in the shutter opening had little effect on the pollutant emissions for the older stove, but had a greater effect on the newer stove. The intermediate air shutter opening (best flame) also had the highest nitrogen oxides levels for the newer stove.

- o Pilot lights, although using gas at a slow rate, do contribute quantities of pollutants comparable to those generated during cooking operations over a typical 24-hour period because of their continuous operation. Pilot light NO and NO₂ emissions from the newer stove were less than those from the older stove. The newer stove also has a pilot light designed to use less gas than the older stove.
- o Evaluation of the number of burners in use and their flame intensity showed that the emissions are similar for all conditions when adjusted to an equivalent heat input basis. Oven and broiler emissions are somewhat less than those for the burners on the same heat input basis.
- o Total pollutant emissions per unit of time from a gas stove are roughly proportional to the number and type of burners used and the period of use (Cote et al. 1974).

Based on the findings of the field study the investigators concluded the following:

- o Indoor NO₂ concentrations in the kitchens of most houses would exceed the National Ambient Air Quality Standard for NO₂ of 100 ug per m³ annual average (if the concentrations were projected over 1 year). Average kitchen NO₂ concentrations for most sampling periods were two to four times the outdoor NO₂ concentrations.
- o The half-life for NO was 1.8 hours, indicating its high stability indoors. On the other hand, NO₂ had a half-life of 0.6 hours indicating that it is lost not only to dispersion and dilution, but also through reaction, absorption, or adsorption.
- o Stove pilot lights were found to be a significant source of NO₂ (Cote et al. 1974).

Another study of air pollution in a house with a gas stove found significantly higher indoor kitchen concentrations of NO₂ (Eaton et al. 1972). It found peak NO₂ values of 1 ppm (1,880 ug per m³)

with 1-hour averages ranging from 0.25 to 0.5 ppm (470 to 940 ug per m³) when the kitchen was closed with no ventilation. The gas flow was 0.204 ft³ per minute, and the sampling intake was 6 feet from the stove.

The study conducted at the Lawrence Berkeley Laboratory, mentioned above, measured not only sulfur dioxide, but also NO and NO₂ emissions with the gas oven operating at 550°F (287°C) for approximately 20 minutes (Hollowell et al. 1976). The results were:

<u>Pollutant</u>	<u>Ventilation Conditions</u>		
	<u>No Duct, Fan Off</u>	<u>No Duct, Fan On</u>	<u>Duct, No Fan</u>
NO (ug/m ³)	2,000	1,000	150-500
NO ₂ (ug/m ³)	850	320	95-150

The study also illustrated the effects of gas surface burner conditions on gaseous emissions of NO and NO₂, observing the following levels:

<u>Stove Condition</u>	<u>Pollutant</u>	
	<u>NO (ug/m³)</u>	<u>NO₂ (ug/m³)</u>
Kitchen background	25-85	30-85
One burner on, no grate	165-1,260	115-450
One burner on with grate	125-1,100	65-380
One burner on with grate and all stainless steel pans	160-740	125-380

Such variations in NO_x emissions are due to differences in sampling point locations, gas fired appliances, air-fuel ratios, and dwellings.

The relationship between indoor nitrogen dioxide pollution and heating was studied in Japan (Kogai 1976). In winter, the indoor NO₂ level was higher than the outdoor level. The kitchen level was the highest of indoor levels. The average NO₂ level found in 126 kitchens was 238 ug per 100 cm² per day, which was 10 times more than the outdoor NO₂ level of 22 ug per 100 cm² per day in Japan. The NO₂ level in rooms decreased as the distance between the room and the kitchen increased.

Carbon Monoxide. A literature review by Benson and associates (1972) concluded that indoor carbon monoxide (CO) concentrations appear to follow a pattern similar to those of sulfur dioxide. Indoor concentrations of CO ranged from 80 to 100 percent of outdoor concentrations when outdoor concentrations were below 10 ppm. They ranged from 60 to 80 percent when outdoor concentrations were above 10 ppm. Carbon monoxide is a reactive, odorless gas with a half-life of 2.1 hours. A General Electric Company study (1972) found that the variation in the ratios of indoor to outdoor CO concentrations can be explained by variables such as traffic conditions, nontraffic-related sources, meteorological conditions, and site configurations. This finding is strengthened by another study in which the relationship between CO emissions from gas stoves and from several variables was measured and measurements were made of indoor and outdoor CO concentrations (Yocum et al. 1974).

Still another study was conducted in Hartford, Connecticut (Cote et al. 1974). It suggested that the ovens of new stoves emit about three times as much CO as older stove ovens, but pilot lights on older stoves emit more CO than those on newer stoves. The gas stoves tested emitted 400 to 1,000 ug per Kcal of CO (1,000 to 4,000 mg per hour).

The Hollowell study (1976), mentioned above, shows carbon monoxide concentrations ranging from 2,000 to 2,300 ug per m³ under varying venting duct and fan conditions. It provides data on CO concentrations in the breathing zone under various operating conditions of the top burners of a gas stove as indicated below:

<u>Stove Condition</u>	<u>CO (ug/m³)</u>
Kitchen background	1,000-9,000
One burner on, no grate	2,000-10,000
One burner on, with grate	3,000-9,000
One burner on with grate and all stainless steel pans	3,000-27,000

Such a large spectrum of CO concentrations is due to the different variables suggested for NO_x levels.

An early German study suggested that oil and gas-fired furnaces generate negligible amounts of CO (Baum 1972).

Radioactive Materials. Recently, the Federal Radiation Policy Council warned that indoor exposure to radon is a nationwide problem that threatens to grow worse and requires immediate steps to assess the magnitude of the problem and control options (General Electric Company 1972). Although this has been recognized as a problem only recently, indoor radon is thought to come from airborne radon and radon daughter products found in groundwater supplies used in the home and in masonry construction materials such as concrete and gypsum blocks. About half the radon present in household water supplies becomes airborne. In fact, after radon-rich groundwater is sprayed through a showerhead, concentrations in bathroom air can approach occupational limits (National Academy of Sciences 1980).

However, oil and gas can make a significant contribution to indoor radon levels. The average annual dose equivalent rate for persons who cook with gas ranges is six to nine. For persons exposed to unvented heaters, the average dose equivalent is 22 mrems per year. The bronchial lining is the most affected part of the body. The dose equivalents are the highest (next to smoking) of these for any other consumer product (including outdoor combustion of fossil fuels, luminous compounds, television sets, and construction materials) (National Academy of Sciences 1980).

Natural gas contains about 10 to 20 pCi per liter of radon. This contributes less than 10^4 Ci per year to the worldwide inventory of 40 MCi. The dose equivalent to the lungs of persons using natural gas ranges in the home has been calculated to be about 2 percent of the normal, natural background dose equivalent from radon and its daughters. On this basis, the resulting dose equivalent rates to persons in homes using natural gas for cooking would be about two mrem per year to the alveolar region and nine mrem per year to the segmented bronchial region of the lung (National Council on Radiation Protection and Measurements 1977).

Assuming that about 41 million households use natural gas and there are 3.1 persons per household, the total number of persons exposed to radon from natural gas ranges within U.S. homes is estimated at about 125 million. This means the average annual bronchial lining dose equivalent is about 5 mrem (National Council on Radiation Protection and Measurements 1977).

High ventilation rates would reduce the indoor concentration of radon. For example, four air changes per hour with outside air at 70 pCi/m³ would drop a room concentration from over 4,000 pCi/m³ to less than 80 pCi/m³. This drop is possible because normal emanation does not supply radon fast enough to replace the amount removed. Thus, for normal building materials without extensive unvented indoor oil and gas combustion, indoor concentrations of radon are probably

high only in closed or poorly ventilated areas (National Council on Radiation Protection and Measurements 1975).

This presents a serious conflict with a national goal of energy conservation and energy efficient homes. With a well insulated, tightly closed house, radon released from the burning of natural gas may attain levels high enough to warrant concern for human health.

Emissions from Space Heaters

Residential emissions from oil and gas combustion are listed in Table 12. The data include emissions from residential cooking, space heating, and water heating. It is assumed that approximately 75 percent of residential natural gas consumption is for water heating and cooling and that 95 percent of distillate oil consumption is for space heating (Helfand 1977). The data indicate that, except for emissions of nitrogen oxides (NO_x) and carbon monoxide (CO), natural gas is a "cleaner" fuel than oil. For NO_x , and to a limited extent CO, the ratio of gas to oil emissions is proportionate to the number of units (two to one). Relative to national emissions, the pollution contribution of space heating systems appears small. However, by nature, residential heating emissions are concentrated during winter, and occur in populated areas. The ratio of NO to NO_2 has been found to be about nine to one in residential heating systems. From an indoor air pollution standpoint these NO_x emissions, if escaping from faulty emission control systems, could have a severe impact on human health during the winter season. (See the above discussion of gas stoves and ovens for additional information on emissions from space heaters.)

Research needs related to the behavior of these indoor pollutants are discussed below in the section on the transport and transformation effects of indoor air pollutants generated as a result of the combustion of oil and gas for home heating and cooking.

Mobile Source Emissions

Automobile emissions result from burning gasoline or diesel fuel in internal combustion engines, as well as evaporation from crankcase leakage, engine head, storage tank, and carburetor. Significant exhaust emissions include particulate matter, CO, NO_x , SO_2 , HC, and aldehydes. These are considered to pose the greatest health hazard and to warrant detailed identification and characterization. Because of their widespread use in light duty, automobiles are responsible for a large share of air pollutant emissions in many areas of the U.S. EPA's Emission Factor Program (EFP) estimates emission levels of in-use vehicles. The program showed that, during 1970, internal combustion engines were responsible for approximately

TABLE 12

SUMMARY OF EMISSIONS FROM RESIDENTIAL GAS AND OIL COMBUSTION
(1973)

Fuel	Particulates	Sulfur Oxides	Nitrogen Oxides (as NO ₂)	Hydrocarbons	Carbon Monoxide
Distillate oil					
(10 ³ metric tons/yr)	77	245	94	23	37
(10 ³ short tons/yr)	70	223	85	21	34
Natural gas					
(10 ³ metric tons/yr)	23	2	185	19	46
(10 ³ short tons/yr)	21	2	168	17	42
Total national emissions ^a					
(10 ³ metric tons/yr)	18,110	36,144	24,023	26,687	109,421
(10 ³ short tons/yr)	16,464	32,859	21,839	24,261	99,474

^aTotal includes emissions from all sources.

Source: Hefland 1977.

73 percent of carbon monoxide, 56 percent of hydrocarbons, and 50 percent of nitrogen oxides emitted in the U.S. (U.S. Environmental Protection Agency 1977a). Automobiles also contributed 2.5 percent of the total particulates and 3.4 percent of the sulfur dioxides. These percentages have been significantly reduced as a result of emission control devices, engine modifications, and changes in fuel composition, although there are more vehicles on the road. Table 13 summarizes exhaust emission rates.

Particulate Emissions

Several parameters, such as fuel composition, engine design and maintenance, operating conditions, and emission control devices, may influence the physical characteristics of particulates emitted from diesel engines. The particle size, number, surface area, and settling velocity determine the potential for adsorptive capacity and airborne characteristics. The physical characteristics of particles from diesel exhaust are presented below (U.S. Environmental Protection Agency 1978c).

<u>Parameter</u>	<u>Value</u>
Mass medium diameter	0.1 - 0.3 μm
Particulate count	107 count/ cm^3
Surface area	2 m^2/m^3
Settling velocity	0.25 - 40 mins/hr

The particulate size distribution and mass output in diesel engine exhausts were measured in a study which showed that particulate concentrations ranged from 14.2 to 250.9 mg per m^3 and mass outputs from 52 to 3,443 mg per minute (Breslin et al. 1976). Statistically significant differences were found to occur with different engine types, fuels, and operating modes.

According to scientists in the General Motors Research Laboratories, engine oil contributes 1.5 to 25 percent by mass of diesel particulate emissions, depending upon engine speed and load. An increase in load or engine speed increases the engine oil's contribution to the total particulate concentration.

With the exhaust from gasoline engines, particulate size depends on fuel composition. Unleaded fuel results in the emission of larger particles. For leaded fuels, approximately 90 percent by weight of the emitted particles are less than 0.35 μm in diameter and 88 percent by weight have diameters shorter than 10 μm . The particle size

TABLE 13
EXHAUST EMISSION RATES FOR MOBILE COMBUSTION SOURCES

	New Light-Duty Gas Automobiles		New Light-Duty Diesel Vehicle		New Light-Duty Gas Truck		New Heavy-Duty Gas Truck		New Heavy-Duty Diesel Vehicle	
	Model Year	Emission Rate (gm/mile)	Model Year	Emission Rate (gm/mile)	Model Year	Emission Rate (gm/mile)	Model Year	Emission Rate (gm/mile)	Model Year	Emission Rate (gm/mile)
Hydrocarbons ^a	Pre-1968	4.45	Pre-1973	0.46	Pre-1968	4.76	Pre-1970	23.90	Pre-1974	4.30
	1968-1974	2.43			1968-1969	3.25	1970-1973	18.54	1974-1978	4.50
	1975-1979	1.13			1970-1974	2.56	1974-1978	22.02	1979-1982	4.50
	1980+	0.13			1974-1978	1.92	1979-1982	5.22	1983+	2.85
					1979-1982	0.94	1983+	1.46		
Carbon monoxide ^a	Pre-1968	68.30	Pre-1973	1.7	Pre-1968	70.38	Pre-1970	272.90	Pre-1974	35.10
	1968-1974	31.14			1968-1969	42.08	1970-1973	212.70	1974-1978	27.00
	1975-1979	18.60			1970-1974	31.48	1974-1978	218.80	1979-1982	27.00
	1980	3.00			1975-1978	23.44	1979-1982	191.90	1983+	27.00
	1981+	1.40			1979-1982	14.50	1983+	15.38		
Nitrogen oxides ^a	Pre-1968	3.58	Pre-1973	1.6	Pre-1968	4.16	Pre-1970	8.80	Pre-1974	21.40
	1968-1972	4.43			1968-1969	4.90	1970-1973	12.80	1974-1978	20.10
	1973-1974	2.98			1970-1972	4.59	1974-1978	10.50	1979-1982	15.90
	1975-1976	2.42			1973-1974	3.56	1979-1982	9.10	1983+	5.35
	1977-1980	1.50			1975-1978	3.62	1983+	3.99		
Particulates ^b	Pre-1973	0.34	Pre-1973	0.73	Pre-1973	0.34	Pre-1973	0.91	Pre-1973	1.3
Sulfur oxides	Pre-1973	0.13	Pre-1973	0.54	Pre-1973	0.18	Pre-1973	0.36	Pre-1973	2.8

^aSource: U.S. Environmental Protection Agency 1978.

^bSource: U.S. Environmental Protection Agency 1977a (AP-42).

distribution with leaded and unleaded fuels suggests that the weight of the small particles (<0.35 μm diameter) is much higher with leaded than with unleaded fuel (Sampson and Springer 1973). About 71 to 91 percent of the lead particles emitted in exhaust from an automobile using leaded gasoline fall in the respirable size range, compared to 34 to 59 percent with unleaded gas (Mueller 1970). The size of exhaust particles is similarly dependent on the fuel's sulfur content. Mueller (1970) demonstrated that respirable particles in the range of 0.1 to 1.0 μm can stay dispersed in the atmosphere.

The diameter of emitted particles depends not only on fuel composition, but also on engine operating conditions. Habibi et al. (1970) demonstrated that, with leaded fuel, cyclic operations yield larger particles than steady-state operations. They also noted that the average size of the emitted lead particles increases significantly with mileage accumulation, rising from 1.1 μm at 6,530 average mileage to 4.7 μm at 21,350 average mileage. The corresponding effects on particle size for unleaded fuels have not been studied.

Table 14 provides data on particulate emissions from diesel- and gasoline-powered passenger cars, illustrating the effect of catalytic converters on particulate emission rates (U.S. Environmental Protection Agency 1978c). Table 15 shows the effects catalytic converters can have on emissions and Table 16 lists qualitatively summarized data on the effect of different variables on particulate emissions from diesel- and gasoline-powered cars (U.S. Environmental Protection Agency 1978c).

It should be noted that both diesel- and gasoline-powered engines release suspensions of microsize solid particles and liquid droplets in either a gas or vapor phase.

Sulfur Emissions

Sulfur dioxide and sulfate emissions are directly related to the sulfur content of diesel and gasoline fuels. The sulfate emission rates for diesel- and gasoline-powered passenger cars are shown in Table 17. The comparison of the average values shows that diesel cars have higher sulfur emission rates than noncatalyst gasoline cars. However, diesel cars and gasoline cars equipped with a catalyst have comparable sulfate emission rates. These emission rates are substantially lower for advanced noncatalyst and three-way catalyst gasoline-fueled vehicles. The sulfate emission rates for both diesel- and gasoline-powered cars depend on four variables: vehicle design and engine displacement, sulfur content of the fuel, vehicle operation mode, and engine mileage. Emission rates tend to increase in proportion to vehicle size, since larger vehicles consume more fuel.

TABLE 14

PARTICULATE EMISSIONS FROM
DIESEL- AND GASOLINE-POWERED PASSENGER CARS

Vehicle Type	Total Particulates in FTP Mode (mg/mile)
<u>Diesel vehicles</u>	
VW Rabbit	294.0
Peugeot 504	397.0
Mercedes 240D	477.0
Mercedes 300D	490.0
Oldsmobile 350	924.0
<u>Gasoline vehicles</u>	
With emission control	
VW Rabbit	6.8
Oldsmobile 350	9.1
Without emission control	
Leaded gasoline car	246.0
Unleaded gasoline car	181.0
Advanced unleaded gasoline car	2.0

Source: Adapted from U.S. Environmental Protection Agency 1978c.

TABLE 15
EFFECT OF CATALYTIC CONVERTER ON
PARTICULATE EMISSION RATES

Vehicle Type	Particulate Emission Rate (mg/mile)
Light-duty gasoline- powered vehicles:	
Catalyst	6
Catalyst (excess air)	15
Non-catalyst (lead fuel)	250
Non-catalyst (unleaded fuel)	2
Light-duty diesel- powered vehicles:	
Non-catalyst	500
Catalyst	Some small decrease

Source: Adapted from U.S. Environmental Protection
Agency 1978c.

TABLE 16

EFFECT OF VARIABLES ON PARTICULATE EMISSION FROM
GASOLINE- AND DIESEL-POWERED CARS

Variable	Effect on Particulate Mass	
	Diesel	Gasoline
Engine type		
Indirect injection	Increase	---
Direct injection	Decrease	---
Turbocharging	Decrease	---
Engine displacement	Decrease with decrease in parameter	Decrease with decrease in parameter
Emission control		
Exhaust gas re- circulation (EGR)	Increase	---
Catalyst	Increase	Increase
Catalyst and water scrubber	Decrease	---
Thermal reactor	Decrease	---
Engine speed and load ^a	No change in particulate size Increase in mass with in- crease in variable	Decrease in particulate size Increase in mass with in- crease in variable
Engine maintenance		
Engine deterioration	Increase with poor maintenance	---
Combustion chamber deposits		Increase with deposits
Fuel composition		
Sulfur content	Increase with increase in variable	
Aromaticity	Increase with increase in variable	

TABLE 16 (Concluded)

Variable	Effect on Particulate Mass	
	Diesel	Gasoline
Fuel additives		
Lead	---	Increase
Halogen compounds	Increase	Increase
Nitromethane	Decrease	Decrease
La and Ni-additives	Decrease but may decrease engine life	---
Methanol	Decrease	---
Water injected with fuel	Decrease	---
Detergent	Injector stays clean but no hard data on particulate emissions	Increase

Note: --- Represents trend not analyzed.

^aWith gasoline engines, particulate size decreases with an increased engine size and load.

Source: U.S. Environmental Protection Agency 1978c.

TABLE 17
SULFATE EMISSION RATES

Vehicle Type	Emission Rate (mg/mile)
<u>Diesel vehicles</u>	
VW Rabbit	1.7
Peugeot 204D	8.2
Peugeot 504	6.5
Mercedes 220D (comprex)	9.2
Mercedes 240D	14.2
Mercedes 300D	16.6
Oldsmobile 350	21.0
<u>Gasoline vehicles</u>	
Non-catalyst, no air pump	
Chevy, 1972	0.2
Non-catalyst, air pump	
Granada, 1975	0.7
Dodge, 1975	2.7
Catalyst, pelletized, no air	10.1 ^a
Catalyst, pelletized, air	12.8
Catalyst, monolith, no air	7.7
Catalyst, monolith, air	33.5
Advanced non-catalyst	1.9
Advanced catalyst	
Three-way, fuel injected	1.5
Three-way	0.6

^aAverage for 1975-1976 cars.

Source: U.S. Environmental Protection Agency 1978c.

Braddock and Gabele (1977) found that SO₂ and sulfate emissions from the Peugeot are similar to those from the Nissan diesel. Using the average no. 2 diesel test fuel containing approximately 0.23 percent sulfur, they found a sulfate emission rate of 8.9 $\pm$ 1.7 mg per mile for the Peugeot and 7.8 mg per mile for the Nissan diesel.

Carbonyl sulfide, a sulfur-containing compound, is also emitted in diesel exhaust, and emission rates for test vehicles are given below (Braddock and Gabele 1977):

CARBONYL SULFIDE EMISSIONS (mg/mile)

Test*	Type of Vehicle		
	Peugeot <u>Diesel</u>	Honda <u>CVCC</u>	Lean-Burn <u>Chrysler</u>
FTP	0.55+0.15 (N=4)	0.06+0.06 (N=3)	0.40+0.35 (N=4)
FET	0.19+0.22 (N=6)	0.51+0.67 (N=3)	0.26+0.16 (N=3)
SET	0.24+0.14 (N=11)		

This is part of a limited data base currently available and detailed work is needed to develop conclusive data. These data are important to the study of health effects of diesel exhausts.

With gasoline-powered passenger cars, sulfate is emitted as sulfuric acid. A striking increase in the acidity of emitted particles has been observed when gasoline engine exhausts are treated with a catalytic converter (Stara et al. 1974). It has been shown that the acidity of emissions from catalyst-fitted engines is 65 to 260 times greater than that of emissions from engines with no catalytic converters. The sulfate emission composition from diesel-powered automobiles is not known. The sulfuric acid emitted from vehicles is partly neutralized by ammonia to form (NH₄)₂SO₄ and NH₄HSO₄. Part of the acid reacts with other metallic elements in the atmosphere to form metal sulfates. However, it has been estimated that more than 70 percent of the sulfate emitted by vehicles remains in the form of H₂SO₄ at 20 meters downwind from the point of emission (Wilson et al. 1977). This phenomenon is of major importance to the acid rain problem in the U.S.

*These terms are used in the following discussions on mobile emission rates: Federal Test Procedure (FTP), Highway Fuel Economy Test (FET), Sulfate Emissions Test (SET).

Hydrocarbon Emissions

The burning of hydrocarbon fuels under "nonideal" mobile conditions involves complex processes and results in hydrocarbon emissions. In addition, uncombusted fuel and lubricating oil are partially responsible for these emissions. Both absolute and relative concentrations of combustion products are influenced by the fuel-to-oil ratio, ignition timing, inlet mixture density, combustion chamber geometry, and variable parameters such as speed, load, and engine temperature.

Exhaust hydrocarbons can be separated into a particulate phase and a volatile/vaporous phase. The nature of organic emissions adsorbed on particulate phase hydrocarbons emitted from diesel-powered automobiles was determined to range from C₁ to about C₄₀ (Black and High 1978). Hydrocarbons in the C₁ to C₁₀ range result from combustion while the C₁₀ and C₄₀ organics generally originate from uncombusted fuel and lubricant and from partial combustion and rearrangement of compounds. Some of the organics in the range of C₁₀ to C₄₀ are particle bound and some are in the gaseous or volatile phase. Generally, the particle-bound organics range from C₁₄ to about C₄₀, and gas phase organics from C₁ to about C₂₅. The principal sources of these organic particles are uncombusted fuel, partial combustion products, and lubricating oils (Black and High 1979). Black and High (1979) conclude that for organic emissions above C₂₅, lubricating oil must be the principal source since there are no significant fuel components in that range. Both fuel and lubricants contribute those between C₁₄ and C₂₅.

The mix of hydrocarbons in exhaust emissions from gasoline-powered automobiles is generally 50 percent saturated aliphatics, 5 percent PNAs, and 30 percent oxygenated hydrocarbons. The compounds have a molecular weight range of 300 to 500 by GC-MS (Boyer and Laitinen 1975). The aliphatic hydrocarbons include straight chained, branched chain, unsaturated, and small ring compounds; while oxygenated hydrocarbons include the following: diethyl phthalate, di-isobutyl phthalate, di-n-butyl phthalate, triphenyl phosphate, di-n-octyl phthalate, methyl triphenyl phosphate, trimethyl triphenyl phosphate, dimethyl triphenyl phosphate, benzanthrone, suspected B-capryophyllene, benzo[c]-cinnoline, benzoic acid, 2,6-di-tert-butyl hydroquinone or nonylphenol, and a number of unidentified compounds including oxygenated PNAs.

Recently, scientists from General Motors Research Laboratories have suggested that low-molecular-weight aliphatic amines in exhaust are emitted from catalyst-equipped cars. It has been demonstrated (using a 1975 FTP test) that total aliphatic amine emissions amount to less than 2.2 mg per mile and that the average emission rates of

monomethylamine and dimethylamine are no more than 0.3 and 0.1 mg per mile, respectively. The scientists concluded that automotive amine emissions are not high enough to account for nitrosamine concentrations which have been reported at roadway sites (Cadle and Mulawa 1980).

Organic compounds in the range of C₁ to C₄₀ adsorbed on diesel exhaust particulate matter have been detected by Metser and Sharkey (1977) with diesel fuel oil no. 1 and no. 2. These organic compounds are: crotonaldehyde; B-propiolactone; unresolved 2-butanone; tetrahydrofuran; pentane; unresolved ethylformate; 2,3-epoxy-1-propanol; methyl acetate; carbon disulfide; benzene; pyridine; cyclohexane; cyclohexene; methylacrylate; 2-pentanone; hexane; unresolved dioxane; ethyl acetate; toluene; aniline; phenol; furfural; furfuryl alcohol; unresolved mesityl oxide; cyclohexanone; methyl cyclohexane; unresolved cyclohexanol; 2-hexanone; unresolved ethyl acrylate; methyl methacrylate; heptane; styrene; unresolved ethyl benzene; xylene; unresolved monomethylaniline; o-toluidine; cresol; hydroquinone; methylcyclohexanone; allylglycidyl ether; octane; unresolved vinyl toluene; a-methyl styrene; cumene; isophorone; p-ter-butyl toluene; phenylglycidyl ether; camphor; phenyl ether; and dinitro-o-cresol. The lower-molecular-weight compounds in the list have not been reported by other workers. Besides these compounds, sulfur containing compounds, namely benzothiophenes and dibenzothiophenes, have been detected in diesel exhaust (National Institute for Occupational Safety and Health 1978).

Polycyclic Aromatic Compounds. This class of compounds is found in the automotive exhaust, mostly in the particulate adsorbed phase. One group of polycyclic aromatic compounds, the polynuclear aromatic hydrocarbons, has been detected in both diesel and gasoline exhaust. The compounds are believed to result from three sources: (1) incomplete combustion of materials in the fuel, (2) synthesis of aromatic hydrocarbons of lower molecular weight during fuel ignition, and (3) pyrolysis of lubricating oil. Laity et al. (1973) demonstrated the mechanism of their formation in automobile engines. They observed that polynuclear emissions are enhanced by increased heat input in the combustion chamber. The emissions of these compounds from a gasoline-powered car and a diesel-powered omnibus are listed in Table 18. A comparison of emissions from heavy-duty diesel vehicles and typical gasoline automobiles run under urban American driving conditions is provided in Table 19 (U.S. Environmental Protection Agency 1978c). The data on American cars is for older models since current data are not available.

TABLE 18

POLYCYCLIC AROMATIC HYDROCARBONS
DETECTED IN VARIOUS ATMOSPHERIC POLLUTANT SAMPLES

(+= detected; - = not detected)			
Compounds	A	B	C
Naphthalene	+	-	-
Acenaphthylene	+	+	+
Anthracene	+	+	+
Phenanthrene	-	+	-
Anthracene derivatives	+	+	+
Pyrene	+	+	+
Fluoranthene	+	+	+
Alkylpyrene	+	-	-
Benz(a)anthracene	+	+	+
Chrysene	+	-	+
Benzo(e)pyrene	+	+	+
Perylene	+	+	+
Benzo(a)pyrene	+	+	+
Benzo(ghi)perylene	+	+	+
Benzo(b)fluoranthene	+	+	+
Anthanthrene	+	+	+
Tetracene	+	-	-
Coronene	+	+	+
Dibenz(a,h)anthracene	+	-	-
4-Dibenzo(a,l)pyrene	+	+	-
Benzo(k)fluoranthene	+	+	+
Pentaphene	+	+	-
Dibenzo(a,l)naphthacene	+	-	-
Dibenzo(a,h)pyrene	+	-	-
Dibenzo(a,e)pyrene	+	-	-
Dibenzo(b,pqr)perylene	+	-	-
Dibenzofluorene	-	+	+
Tribenzo(h,rst)pentaphene	+	-	-
Indeno-1,2,3-fluoranthene	-	+	-

Notes: A = Gasoline soot.
 B = Diesel soot.
 C = Atmospheric soot.

Source: U.S. Environmental Protection Agency 1978c.

TABLE 19

COMPARISON OF POLYCYCLIC AROMATIC HYDROCARBON EMISSIONS
FROM HEAVY-DUTY DIESEL- AND GASOLINE-POWERED VEHICLES^a

Compound	Emission Rates (µg/gal fuel burned)	
	Diesel Heavy Duty Vehicles	6-Cylinder 1956-1962 American Gasoline-Powered Cars
Anthracene	ND	41
Phenanthrene	6,410	176
Phenanthrene derivatives	8,280	NR
Fluoranthene	253	872
Pyrene	349	1,145
Benz(a)anthracene	35	NR
Chrysene	5	NR
Benzo(J+k)fluoranthene	NR	NR
Benzo(a)pyrene	22	147
Benzo(e)pyrene	4	205
Indeno(1,2,3-cd)pyrene	NR	NR
Benzo(ghi)perylene	7	649
Anthranthrene	NR	27
Coronene	NR	256
Perylene	NR	12

Notes: ND = not detected.

NR = not reported.

^aDiesel fuel with 26 percent aromatics and gasoline fuels with 25 percent aromatics.

Source: Adapted from U.S. Environmental Protection Agency 1978c.

Polynuclear aza heterocyclics make up another class of compounds in automobile exhausts which include the following arenes (Sawicki et al. 1965):

<u>Arenes</u>	<u>Particulate Matter ug/g Exhaust*</u>
Benz(h)quinoline	0.2
Benz(c)acridine	0.4
Indenoquinolines	0.9
Dibenz(9,j)acridine	<0.2
Dibenz(a,h)acridine	<0.2
Alkylbenz(c)acridine	<0.2

Benzo(a)pyrene (BaP) has typically been measured and used in vehicular emission research and air pollution monitoring as an indicator of total concentration of polycyclic aromatic hydrocarbons (PAHs). Consequently, the bulk of available data is in terms of BaP. The use of BaP as an indicator or index of total PNA emissions is questionable.

Analysis of diesel fuels has shown that these tend to contain lower concentrations (up to 422 ppb) of BaP than gasoline (up to 300 ppb) (Lyons 1962). Although one might expect higher concentrations of PAHs in less volatile diesel fuel, gasoline actually contains much higher concentrations of catalytically processed aromatic hydrocarbons. BaP emission levels from diesel and gasoline cars without catalysts are 1.57 ug per mile and 1.95 ug per mile, respectively (Pedco 1978). Use of oxidative catalysts and other pollution control devices has reportedly reduced all emissions from gasoline-fueled engines by about 99 percent. These results have not been confirmed or validated conclusively; thus, they should be interpreted with caution.

The PAHs emissions, like all other exhaust emissions, are dependent on a number of parameters, including: vehicle characteristics and engine design, engine operation mode, engine maintenance, fuel composition, and exhaust emission control systems. BaP emission rates with respect to increasing load with constant speed and

*These data were generated with cars not equipped with a catalyst and may be subject to change.

increasing speed with no load are listed in Table 20. From the data, one can conclude that increasing engine load results in a rapid decrease in BaP emissions in gasoline-powered cars, but results in an increase in BaP emissions in diesel-powered cars.

Deposits in the combustion chamber and fouling of the fuel injection system can dramatically increase PAHs emissions. As much as 6.5 times more BaP can be emitted from gasoline engines with combustion chamber deposit than from cleaner engines (Gross 1972). Diesel engines with chamber deposits due to poor maintenance have a BaP emission rate of 1,706 ug per minute under full load conditions, compared to negligible BaP emissions from a well maintained diesel engines.

An increase in fuel aromaticity results in increased PAHs emissions. Gross (1972) demonstrated that increasing a fuel's aromatic content from 11 percent to 46 percent results in a 124 percent increase in uncontrolled PAHs emissions from gasoline-powered cars. This result has not been conclusively proven.

The effect of lead in gasoline on PAHs emissions is being studied in several laboratories. The effect of gasoline engine mileage on PAHs emissions is shown in Table 21 (Hangebrauck et al. 1967). PAHs emissions are highest from older cars that have traveled more than 50,000 miles.

Emission control devices and engine modifications substantially reduce BaP emissions in gasoline- and diesel-powered automobiles. The reduction has been shown to be 70 to 98 percent for gasoline-powered and 80 to 90 percent for diesel-powered cars (Gross 1972; National Institute for Occupational Safety and Health 1978).

Chlorinated Dioxins. The chlorine content of leaded gasoline is 300 ppm, while that of unleaded gasoline is 1 to 6 ppm (National Academy of Sciences 1976a). The combustion of these fuels could release chlorinated dioxins. To study chlorinated dioxin emissions, Dow Chemical Company tested mufflers from gasoline-powered automobiles and diesel-powered trucks. Muffler particulate solids were analyzed by both GC-MS and GC-EC following liquid chromatography separation. The results of the study are shown in Table 22 (Dow Chemical Company 1978). The dioxins that were present included TCDD (the total of all 22 tetra isomers), HCDD (the total of all 10 hexa isomers), H7CDD (the total of the 2 hepta isomers), and OCDD (octachloro-dibenzo-p-dioxin). More work is needed to study and identify chlorinated dioxins in automobile exhausts.

TABLE 20

BENZO(A)PYRENE EMISSION RATES
($\mu\text{g}/\text{min}$)

Engine Load with Speed at 1,000 Rpm	Emissions		Rpm with no Load	Emissions	
	Gasoline	Diesel		Gasoline	Diesel
0	61	146	500	120	Not reported
1/4	0	465	1,000	61	146
1/2	1	772	1,500	33	Not reported
3/4	0	1,320	2,000	40	Not reported
Full	0	876	2,500	25	Not reported
			3,000	13	Not reported

Source: Adapted from U.S. Environmental Protection Agency 1978c.

TABLE 21

EFFECT OF GASOLINE ENGINE MILEAGE ON POLYCYCLIC
AROMATIC HYDROCARBON EMISSIONS

Car Mileage	PNA Emissions ($\mu\text{g}/\text{mile}$)						
	B(a)P	Pyrene	B(c)P	Perylene	B(ghi)P	Anthranthrene	Coronene
19,000	5.6	81	9.5	0.28	26.0	2.3	9.6
26,000	4.2	70	8.1	0.78	35.0	0.64	10.7
49,000	3.9	27	8.6	0.57	14.3	0.3	4.1
58,000	21.5	119	23.5	1.38	77.0	3.17	32.2

Source: Hangebrauck et al. 1967.

TABLE 22

CHLORINATED DIOXIN CONTENT OF PARTICULATE MATTER IN MUFFLERS

Sample Source	Apparent Dioxins (ppt)							
	TCDD		HCDD		H ₇ CDD		OCDD	
	Other Isomers	2,3,7,8-	GC-MS	GC-EC	GC-MS	GC-EC	GC-MS	GC-EC
Auto mufflers								
#1 non-catalytic	4.0(2.0)	ND (2.0)	ND(14)	NA	ND(6)	3(0.4)	16(8)	10(0.6)
#1 non-catalytic	4.0(2.0)	ND (2.0)	ND(14)	NA	ND(6)	3(0.4)	16(8)	10(0.6)
#5 catalytic carbon	ND(1.0)	ND (3.0)	ND(10)	2.0(0.4)	14(8)	10(0.4)	68	72(1.0)
#5 catalytic rust	4.0	0.4(0.1)	-	0.7(0.1)	+	3(0.1)	+	28(0.4)
#2 catalytic	0.1(0.1)	ND (0.2)	-	0.5(0.1)	+	2(0.2)	+	8(0.5)
Diesel mufflers								
#7	ND(7.0)	ND (3.0)	ND(25)	4.0(2.0)	110(30)	35(2.0)	280	205(3.0)
#6	20	3.0(1.0)	20(15)	37(1.0)	100(15)	49(1.0)	260	190(3.0)

Notes: + = The positive result was confirmed by GC-MS.

- = That GC-MS was unable to confirm the positive result.

NA = Not analyzed.

ND = Not detectable at 2.5 times noise.

Data less than 10 times noise will have a detection limit reported in parentheses.

Source: Dow Chemical Company 1978.

Volatile Phase Compounds. The volatile phase hydrocarbon emissions include low-molecular-weight hydrocarbons, phenols, and aldehydes. (The gaseous hydrocarbons emitted from gasoline- and diesel-powered passenger cars have been discussed.) With the exception of methane and toluene, individual hydrocarbons are emitted at higher levels for diesel than for gasoline cars (U.S. Environmental Protection Agency 1978c). The oxygenated hydrocarbons, including alcohols, ethers, phenols, aldehydes, ketones, esters, peroxides, and organic acids, are emitted from automobiles as vapors during fuel combustion. Table 23 lists some typical oxygenates found in automobile exhaust emissions (Urone 1976). The aldehydes discussed earlier are the major oxygenates in the vapor phase of hydrocarbons. With the exception of crotonaldehyde, diesel cars emit more aldehydes than catalyst-equipped gasoline cars. Many oxygenated compounds are secondary products from photochemical reactions. The aldehydes are carbonyl-containing organic compounds emitted from gasoline- and diesel-powered cars. The emission rates for aromatic aldehydes have been shown to increase from 5.8 to 13.6 ppm, with an increase in the aromatic content of gasoline fuel from 27.3 to 46.6 (molar percent) (Hinkamp et al. 1971). The aromatic content of leaded regular gasoline is 27.3 molar percent. For leaded premium it is 30.8 molar percent; and for unleaded premium gasoline it is 46.6 molar percent. Phenols have also been detected in exhaust gases from gasoline cars. Like aromatic aldehydes, phenols increase with an increase in fuel aromaticity (Gross 1972). Phenol emission ranges are listed in Table 24.

Cyanides and Sulfides. Hydrogen cyanide (HCN) and carbonyl sulfide (COS) are combustion products emitted from diesel- and gasoline-powered cars (Braddock and Gabele 1977). These compounds are emitted at low levels, but more research is needed to define emission rates.

Trace Metals Emissions

Metals in automobile emissions originate from two distinct sources: (1) fuel and lubricating oil, and (2) engine and exhaust system wear. When catalytic converters are used, a third possible source could be products from the catalyst.

When leaded gasoline is used, the predominant metal content in the exhaust is lead, which will be discussed separately. Typical emission factors for metals cannot be derived from baseline characterization of auto exhaust as performed by EPA, but emphasis on the effect of emissions as a function of variation in operating condition is valid. The data in Table 25 reflect this approach because the different test cycles differ significantly in the average speed and variability of the operating mode (U.S. Environmental Protection

TABLE 23

OXYGENATES IN EXHAUST FROM SAMPLE HYDROCARBON FUELS

Oxygenate	Concentration Range (ppm)
Acetaldehyde	0.8-4.9
Propionaldehyde (+ acetone)	2.3-14.0
Acrolein	0.2-5.3
Crotonaldehyde (+ toluene)	0.1-7.0
Tigaldehyde	<0.1-0.7
Benzaldehyde	<0.1-13.5
Tolualdehyde	<0.1-2.6
Ethylbenzaldehyde	<0.1-0.2
O-Hydroxybenzaldehyde (+ G ₁₀ aromatic)	<0.1-3.5
Acetone (+ Propionaldehyde)	2.3-14.0
Methyl ethyl ketone	<0.1-1.0
Methyl vinyl ketone (+ benzene)	0.1-42.6
Methyl propyl (or isopropyl) ketone	<0.1-0.8
3-Methyl-3-buten-2-one	<0.1-0.8
4-Methyl-3-penten-2-one	<0.1-1.5
Acetophenone	<0.1-0.4
Methanol	<0.1-0.6
Ethanol	0.1-0.6
(5 alcohol (+ C ₈ aromatic)	<0.1-1.1
2-Buten-1-ol (+ C ₈ H ₁₈ O)	<0.1-3.6
Benzyl alcohol	<0.1-0.6
Phenol + cresoles	<0.1-6.7
2,2,4,4-Tetramethyltetrahydrofuran	<0.1-6.4
Benzofuran	<0.1-2.8
Methyl phenyl ether	<0.1
Methyl formate	<0.1-0.7
Nitromethane	<0.8-5.0
C ₄ H ₈ O	<0.1
C ₅ H ₆ O	<0.1-0.3
C ₅ H ₁₀ O	<0.1-0.3

Source: Urone 1976.

TABLE 24
PHENOL RANGE IN GASOLINE EXHAUST GAS
(mg/gal)

Vehicle	11% Aromatic Fuels	28% Aromatic Fuels	46% Aromatic Fuels
1966, no emission control	110 - 1979	279 - 435	653 - 776
1968, engine modification	78 - 165	314 - 406	535 - 691
1970, engine modification with spark retard	74 - 123	222 - 287	370 - 485
1968, an in- jected RAM thermal reactor	-	-	2
1970, catalyst equipped	-	-	2

Source: Gross 1972.

TABLE 25

EMISSION RATES OF SELECTED METALS FROM A VARIETY
OF CARS UNDER DIFFERENT OPERATING CONDITIONS

Cars	Pb (mg/mi)	Mn (mg/mi)	Cu (mg/mi)	Fe (mg/mi)	Ni (mg/mi)
Pre-catalyst (60 mph cruise)					
FTP	40.5	NA	NA	NA	ND
FET	19.8	NA	NA	NA	ND
SET	20.0	NA	NA	NA	NA
Catalyst (49-state standard) (50 mph cruise)					
Mean	0.028	NA	0.016	0.029	NA
Median	0.015	NA	0	0.007	NA
Range	0-0.325	NA	0-0.293	0-0.341	NA
Catalyst (Calif. standard)					
FTP	0.03	ND	0.18	2.28	0.01
Dual catalyst					
FTP	0.18	NA	0.12	0.56	4.12
FET	0.03	NA	0.01	0.03	0.27
SET	0.07	NA	0.02	0.07	0.50
Lean burn engine					
FTP	6.69	0.05	0.06	1.17	ND
FET	3.76	0.12	0.08	0.07	ND
SET	7.00	0.07	0.08	0.15	ND
Stratified charge					
FTP	ND	ND	ND	0.13	0.01
FET	ND	ND	ND	0.23	0.01
SET	0.12	0.01	ND	0.05	ND
Rotary					
FTP	0.40	0.09	0.04	0.70	0.06
Diesel (#2 national average fuel)					
FTP	2.55	1.46	1.56	1.56	NA
FET	2.50	1.45	2.03	0.12	NA
SET	2.00	1.19	1.54	0.08	NA

Notes: NA = Not available.
ND = Not detectable.

Source: U.S. Environmental Protection Agency 1978c.

Agency 1978c). More research is needed to establish the possible trace metal emission rates with both diesel- and gasoline-powered passenger cars. Sulfur, lead, manganese, and copper are elements of particular prominence from diesel-powered passenger cars in amounts related to fuel composition and combustion. Calcium, phosphorous, and iron emissions appear to be related to lubricating oil consumption, and engine and exhaust system wear. Nickel is present only in trace quantities (U.S. Environmental Protection Agency 1978c; Braddock and Gabele 1977).

Lead in Gasoline

In 1975, atmospheric emissions of lead in the U.S. totaled 155,900 tons, and 90.4 percent of that amount was from gasoline combustion (U.S. Environmental Protection Agency 1977a). Although gasoline sales have increased since then, lead emissions from gasoline combustion have probably declined as Federal law forced the lead content of gasoline to be reduced from 0.45 ug per liter to 0.13 ug per liter by 1979. In fact, the 1975 level of lead emissions is expected to be reduced by 58 percent in 1985. Lead compounds such as lead halides and lead oxyhalides are emitted only with leaded gasoline.

The antiknock compounds tetraethyl and tetramethyl lead are added to gasoline to increase its octane rating. There is a non-linear relationship between gasoline lead content and octane number. The antiknock quality of gasoline is primarily controlled by the chemical composition of hydrocarbons in the gasoline. The lead alkyls suppress knocking by varying the chemical composition. Not all lead contained in fuel is emitted in the exhaust system from a gasoline engine; some is retained in the engine, exhaust system, and the crankcase oil.

The following are conclusions derived from EPA investigations:

- (1) A large portion of the lead (approximately 40 to 75 percent) generated by engines burning leaded fuel is in particles of submicron size, with mass median equivalent diameters in the order of 0.1 to 0.3 μm .
- (2) Lead compounds accumulate in crankcase oil and on components of the engine and exhaust system. Over the life of an automobile about 75 percent of the lead in fuel is emitted as particulate matter in the exhaust.

- (3) In general, 40 to 75 percent of the lead emitted from production vehicles in typical operation modes is in fine particles, i.e., in particles with diameters of less than 1 μm . This suggests that, on the average, 35 to 40 percent of lead in fuel is emitted as fine particulates. About an equal amount (35 to 40 percent) must then be emitted as coarse particles. The emission rate of coarse particles is greatly influenced by reentrainment of lead compounds that have been deposited in the exhaust and is highly variable; fine particles are likely to be those emitted directly from the engine at a rate more uniform than that of large-particle emissions (U.S. Environmental Protection Agency 1977a).

The inorganic lead compounds identified from lead trap deposits in the exhaust from engines burning leaded fuel include PbSO_4 , PbBr_2 , $\text{Pb}_3(\text{PO}_4)_2$, and PbO . These inorganic lead compounds account for about 84 percent of potential particulate lead exhaust emissions from vehicles (Kunz et al. 1975). Along with these inorganic lead compounds, exhausts also contain Fe_2O_3 , soot, and carbonaceous material. The amount of inorganic lead compounds in exhaust emissions is a function of exhaust gas temperature and the amount of lead in the gasoline.

Nitrogen Oxides Emissions

Nitrogen oxides (NO_x) are formed during mobile combustion of automotive fuels. Nitric oxide (NO) is produced in the high temperature of the combustion zone. The amount of NO emitted is a function of temperature as well as the rate at which the combustion mixture cools. The proper reducing catalyst can expedite decomposition to nitrogen and oxygen and can control NO_x emissions (Hurn 1968). In exhaust gases where higher concentrations and temperatures prevail, some NO is oxidized to nitrogen oxide. The amount of NO_x produced is a function of the ratio of the air-to-fuel mixture used for the engine. At low air-to-fuel ratios, nitrogen oxide emissions are low. At higher air-to-fuel ratios, the temperature of the combustion flame becomes hotter and the nitrogen oxides increase until the air-fuel ratio is greater than the stoichiometric point, and then decrease rapidly as excess air cools the flame (Urone 1976).

The concentration of nitrogen oxides in exhaust is most heavily influenced by peak combustion temperatures and by oxygen availability at the fixation temperature. Reduction in either reduces NO_x levels and the effects are additive. Diesel exhausts contain significant amounts of nitric oxide. The concentration levels are deceptively low if compared with similar data from gasoline auto exhausts. This is because diesel engines are operated with an unthrottled air intake

and induct large quantities of excess air that dilute the combustion products. Comparable dilution does not occur with spark-ignited engines that operate with the intake throttled and with fuel metered in proportion to air flow to maintain the air-fuel ratio within a narrow range of values. Table 26 summarizes gaseous emissions data relating to diesel-powered and gasoline-powered cars for NO_x and CO. The NO_x emission rates for the gasoline cars are higher than for diesel cars in all modes of cyclic operation (U.S. Environmental Protection Agency 1978c).

Carbon Monoxide Emissions

The emission of carbon monoxide also is a function of air-fuel ratio. At the air-fuel ratio of approximately 14.5 pounds of air per pound of a typical gasoline, carbon monoxide emission is near zero. Advances in engine design beyond 1968 models have achieved low CO emission without sacrificing drivability and performance. Typically, concentrations of CO in exhaust emissions are high during the engine idle mode and decrease as the engine speed is increased beyond idle range. At a speed of 5 mph, the carbon monoxide level is 7 percent; at 20 mph, it is 3.1 percent; and at 60 mph it is 1.8 percent (Hurn 1968). Thus, a car's total CO emissions will be influenced by the amount of time spent idling and driving at low speeds. Table 26 summarizes emissions data for carbon monoxide. The CO emissions rates for both diesel- and gasoline-powered cars are about equal, with gasoline cars emitting more CO in the FTP and less in the FET and SET modes than diesel cars.

Smoke and Odor

Smoke and odor pollution is a phenomenon associated with diesel-powered engines.

Smoke. Diesel smoke is classified in three categories: black, blue, and white. Black smoke results from incomplete combustion of the diesel fuel due to fuel injection irregularity or overfueling the engine. Blue smoke results from excessive oil consumption and indicates an engine problem. White smoke represents unburned fuel and is generally associated with cold engine malfunction. Black smoke indicates a significant problem with diesel engines. Good maintenance practice and rapid correction of engine problems are obvious tactics to control such pollution.

Unfortunately, well-maintained diesel engines also discharge black smoke. Fuel additives (catalysts) such as barium-based materials are highly effective in suppressing diesel smoke. The smoke suppressant additives are typically oil-soluble, fully miscible, metallic, or organic liquids. The effect of these additives on

TABLE 26
GASEOUS EMISSION DATA FOR DIESEL-POWERED
AND GASOLINE-POWERED CARS

Vehicle	Emission Rates (g/k)					
	CO			NO _x		
	FTP	FET	SET	FTP	FET	SET
Diesel-powered						
Mercedes 220D	0.81	0.48	0.55	0.65	0.56	0.57
Mercedes 240D	0.60	0.38	0.45	0.79	0.80	0.78
Mercedes 300D	0.53	0.36	0.39	1.07	0.99	0.98
Peugeot 204D	1.06	0.57	0.71	0.42	0.34	0.33
Peugeot 504D	0.88	0.37	0.51	1.63	1.20	1.33
Nissan 220C	1.10	NA	NA	1.37	NA	NA
Oldsmobile	1.24	0.63	0.79	0.70	0.59	0.59
VW Rabbit	0.49	0.31	0.34	0.54	0.52	0.50
Gasoline-powered						
1977 Catalyst equipped Oldsmobile Cutlass	1.34	0.12	0.53	0.85	0.88	0.86
1977 Catalyst equipped VW Rabbit	2.30	0.03	0.19	0.63	1.22	1.01
1970 Mercedes (no catalyst)	20.50	NA	NA	2.19	NA	NA
1968 Air-injected RAM thermal reactor vehicle	2.60	NA	NA	1.18	NA	NA
1970 Catalyst equipped car	4.96	NA	NA	0.43	NA	NA

Note: NA = Not applicable.

Source: U.S. Environmental Protection Agency 1978c.

engine emissions is negligible, and the toxicity of emitted barium (especially of barium sulfate) is not fully understood.

Odor. Specific odorants in diesel exhaust are commonly associated with the broad family of oxygenates. Various additives have been used experimentally to inhibit diesel odor, but the results have been inconclusive. Some diesel exhaust components that are responsible for odor formation have been (O'Donnell and Dravnieks 1970) determined with high resolution chromatography. These odorants are acetaldehyde, n-butanol, decane, methyl benzene, C5 substituted benzene, allyl toluene, methylinden, benzaldehyde, naphthalene, and methyl naphthalene. Other diesel exhaust odorants, identified as a large number of aromatic compounds by Arthur D. Little Company researchers, are listed in Table 27 (Spicer and Levy 1975).

Aircraft Emissions

Gas turbines of aircraft jet engines emit hydrocarbons, carbon monoxide, and nitrogen oxides. Estimates of these emissions are presented in Table 28 (Hurn 1968).

Overall, aircraft cannot be considered a significant source of ground-level pollution, but they may present local nuisances or aggravate air pollution in the vicinity of airport operations. There is some question as to the effect of emissions of high flying aircraft on the quality of the stratosphere and on ozone.

In addition to the gaseous emissions mentioned above, aircraft turbines present a smoke problem that became serious in the late 1960s at major airports in the United States and Europe. Dense jet engine smoke was first associated with water injection used for power boost on takeoff, but dry engines, subsequently developed, have retained the smoke problem. Fuel characteristics, including the presence of aromatic hydrocarbons, markedly influence the amount of smoke generated by an aircraft. The fuel's aromatic content is generally limited to 25 percent to control carbon deposition and smoke generation.

The exhaust emission characteristics of today's aircraft turbine engines are illustrated in Figure 8 (Bahr 1971). The peak CO and HC emission levels occur when the engine is idling or operating at low power. In some engines, particulate emissions are detected in visible concentrations of smoke, particularly at takeoff. Although not generally regarded as a significant health hazard, these visible smoke particulate emissions are undesirable and can result in dirt and visibility problems in and around busy airports.

TABLE 27
DIESEL EXHAUST ODORANTS^a

Compound	Composition	Odor Note
Methylindan	$C_{10}H_{12}$	Irritation
Tetralin	$C_{10}H_{12}$	Rubbery sulfide
Dimethylindan	$C_{11}H_{14}$	Kerosene
Methyltetralin	$C_{11}H_{14}$	Naphthenate
Dimethyltetralin	$C_{12}H_{16}$	Kerosene
Trimethylindan	$C_{12}H_{16}$	Kerosene, irritation
Alkyltetralin	$C_{12}H_{16}$	Kerosene
Trimethyltetralin	$C_{13}H_{18}$	Irritation
Alkyltetralin	$C_{13}H_{18}$	Kerosene, pungent, acid
Alkylindene	$C_{12}H_{14}$	Heavy oil
Alkylindene	$C_{13}H_{16}$	Heavy oil
Monomethyl naphthalene	$C_{11}H_{16}$	Mothball, irritation

^aOdorants noted by the Arthur D. Little Company.

Source: Spicer and Levy 1975.

TABLE 28

AIRCRAFT TURBINE EMISSIONS^a

Engine Mode	Emissions					
	Hydrocarbons		NO _x		Aldehydes	
	Concentration (ppm)	Mass (lbs/hour)	Concentration (ppm)	Mass (lbs/hour)	Concentration (ppm)	Mass (lbs/hour)
Idle	150	20	5	2	5	2
Cruise	5	2	50	45	1	1.5
Takeoff	2	1	5	5	Trace	Nil

^aIncludes emissions from engines in the 15,000-pound thrust category.

Source: Hurn 1968.

FIGURE 8
TYPICAL AIRCRAFT TURBINE ENGINE EXHAUST
EMISSIONS CHARACTERISTICS

In addition, any emissions that are generated during cruise operations are generally dispersed over wide geographic areas. In view of these considerations, aircraft turbine engine exhaust emissions during cruise operations may not be a significant health concern. However, this view is not held by many scientists, some of whom believe that these emissions may have a negative impact on the upper atmosphere.

Table 29 shows the length of time spent by various kinds of planes in each phase of the landing and takeoff cycle at a metropolitan airport. The average level of any given exhaust emission may be defined as the average value resulting from all aircraft within the metropolitan area that taxi, idle, takeoff, climb-out to 3,500 feet, approach from 3,500 feet, land, and taxi back. For any particular exhaust constituent, the average emission level determined in this manner is a more suitable value for assessing the impact of aircraft operations on the airport environment than the peak emission level, which reflects only very specific engine operating conditions. Emission factors for aircraft operation are listed in Table 30. Taxi, idle, and approach times are worst in the most congested, and generally most polluted metropolitan areas.

Locomotive Engines

The primary emissions produced by locomotive diesel engines are smoke, NO_x , HC, and CO. Smoke is recognized as a nuisance that is not a potential health hazard (toxic particulate matter is treated separately). Nitrogen oxides are the only gaseous pollutants emitted from diesel engines at levels approaching those from gasoline engines. Diesel engines emit HC and CO at low levels (compared to gasoline engines) and these levels have been further reduced by various control techniques.

NO_x formation is a function of combustion temperature, oxygen availability, and of the time that conditions favorable to NO_x formation exist in the cylinder. Thus, NO_x formation is intimately related to the combustion efficiency of diesel engines. In other words, the greatest quantity of NO_x is usually formed when the engine attains maximum efficiency and minimum fuel consumption.

The concentration of unburned hydrocarbons in diesel exhaust is determined more by design and performance of the injection system, and by combustion chamber geometry, than by operating variables such as engine speed and load. CO concentration is a function of malfunctions or changes in the operating mode that increase the fuel-to-air ratio. An increase in black smoke is due to an increased fuel-to-air ratio, while increased white smoke is due to bad maintenance, low speed, and low temperature operations. Improved engine components

TABLE 29

TYPICAL TIME FOR A LANDING
AND TAKEOFF CYCLE AT A METROPOLITAN AIRPORT

Aircraft ^a	Time in Mode (minutes)				
	Taxi-Idle	Takeoff	Climbout	Approach	Taxi-Idle
Jumbo jet (3-4)	19.00	0.70	2.20	4.00	7.00
Long range jet (4)	19.00	0.70	2.20	4.00	7.00
Medium range jet (2-3)	19.00	0.70	2.20	4.00	7.00
Air carrier turboprop (2-4)	19.00	0.50	2.50	4.50	7.00
Business jet (2-4)	6.50	0.40	0.50	1.60	6.50
General aviation turboprop	19.00	0.50	2.50	4.50	7.00
General aviation piston (1)	12.00	0.30	4.98	6.00	4.00
Piston transport (4)	6.50	0.60	5.00	4.60	6.50
Helicopter (2)	3.50	0	6.50	6.50	3.50
Military transport	19.00	0.50	2.50	4.50	7.00
Military jet	6.50	0.40	0.50	1.60	6.50
Military piston	6.50	0.60	5.00	4.60	6.50

^a Numbers in parentheses identify the number of engines per aircraft.

Source: U.S. Environmental Protection Agency 1977b.

TABLE 30
EMISSION FACTORS PER AIRCRAFT LANDING
AND TAKEOFF CYCLE

Aircraft	<u>Solid Particulates</u> (lbs)	<u>Sulfur Oxides</u> (lbs)	<u>Carbon Monoxide</u> (lbs)	<u>Hydrocarbons</u> (lbs)	<u>Nitrogen Oxides (NO_x as NO₂)</u> (lbs)
Jumbo jet	1.3	1.82	46.8	12.2	31.4
Long range jet	1.21	1.56	47.4	41.2	7.9
Medium range jet	0.41	1.01	17	4.9	10.2
Air carrier turboprop	1.1	0.4	6.6	2.9	2.5
Business jet	0.11	0.37	15.8	3.6	1.6
General aviation turboprop	0.2	0.18	3.1	1.1	1.2
General aviation piston	0.02	0.014	12.2	0.4	0.047
Piston transport	0.56	0.28	304	40.7	0.4
Helicopter	0.25	0.18	5.7	0.52	0.57
Military transport	1.1	0.41	5.7	2.7	2.2
Military jet	0.31	0.76	15.1	9.93	3.29
Military piston	0.28	0.14	152	20.4	0.2

Source: U.S. Environmental Protection Agency 1977c.

such as a change in fuel injection; use of governors, turbochargers, piston and cylinder liners; alteration of injection timing; changes in engine operation and other engine modifications reduce emissions from diesel engines (Storment et al. 1975). Emission factors associated with locomotive engines are listed in Table 31.

Summary of Mobile Emissions

The important gaseous emissions from mobile source combustion are hydrocarbons (including aldehydes), carbon monoxide, and nitrogen oxides. Emission estimates for a 30-year period from 1955 to 1985 were projected prior to the enactment of the Clean Air Act Amendments of 1970 (National Petroleum Council 1971). These estimates are listed in Table 32. A downward emissions trend was projected, and by 1985 the peak reached between 1965 and 1970 was expected to be reduced by approximately 80 percent for hydrocarbons, 60 percent for carbon monoxide, 45 percent for nitrogen oxides, and 40 percent for particulate matter. The lower hydrocarbon and nitrogen oxides emissions were expected to reduce the incidence of photochemical smog. Table 33 provides 1970 to 1977 estimates of hydrocarbon emissions from highway vehicles.

Historically, various automobile modifications have been proposed to reduce automobile emissions in the U.S. Listed in Table 34, they include recirculation of crankcase and exhaust gases, leaner fuel mixtures, changes in timing and spark ignition, decreased compression ratios, and catalytic exhaust recombiners (Loftness 1978).

Table 35 details proposed automobile emissions standards by the years in which they would take effect (Council on Environmental Quality 1976, 1977). These proposed standards would help reduce air pollution caused by automobile emissions.

Data in a National Petroleum Council report (1971) indicate that hydrocarbon and carbon monoxide emissions from trucks and buses will deviate only slightly from peaks reached in 1970, while nitrogen oxides and particulate emissions will remain constant. The authors of the report suggest that emissions estimates could prove to be high if the use of diesel engines is greater than that assumed in their study. Recent trends, unknown to the authors in 1971, indicate that this may be the case.

Aircraft emissions produced below 35,000 feet from air carriers and general aviation operations are expected to increase. Redesigning and retrofitting jet engine combustors would significantly reduce the smoke problem.

TABLE 31
EMISSION FACTORS BY LOCOMOTIVE ENGINE CATEGORY

Pollutant	2-Stroke Supercharged (switch locomotive)	4-Stroke (switch locomotive)	2-Stroke Supercharged (long distance locomotive)	2-Stroke Turbocharged (long distance locomotive)	4-Stroke (long distance locomotive)	Average Emissions Based on Nationwide Statistics
Carbon monoxide						
lbs/10 ³ gal	84	380	66.0	160.0	180	130
kgs/10 ³ liter	10	46	7.9	19.0	22	16
Hydrocarbons						
lbs/10 ³ gal	190	146	148.0	28.0	99	94
kgs/10 ³ gal	23	17	18.0	3.4	12	11
Nitrogen oxides (NO _x as NO ₂)						
lbs/10 ³ gal	250	490	350.0	330.0	470	370
kgs/10 ³ liter	30	59	42.0	40.0	56	44

Source: U.S. Environmental Protection Agency 1977b.

TABLE 32
ESTIMATED EMISSIONS FROM MOBILE EQUIPMENT
(millions of tons per year)

	1955	1960	1965	1970	1975	1980	1985
Hydrocarbons							
Autos	9.9	12.0	13.0	11.0	5.9	2.4	0.9
Trucks and buses	1.2	1.4	1.7	1.9	1.7	1.4	1.4
Aircraft	0.3	0.3	0.2	0.3	0.2	0.1	0.1
Off-highway	0.7	0.7	0.7	0.6	0.6	0.6	0.5
Total	12.1	14.4	15.6	13.8	8.4	4.5	2.9
Carbon monoxide							
Autos	37.3	45.7	55.2	54.3	40.6	24.3	12.7
Trucks and buses	11.1	12.7	15.6	17.4	16.2	14.0	14.2
Aircraft	2.2	1.4	0.9	0.4	0.5	0.7	0.8
Off-highway	6.7	6.8	5.7	5.3	5.5	4.4	3.4
Total	57.3	66.6	77.4	77.4	62.8	43.4	31.1
Nitrogen oxides							
Autos	3.3	4.0	4.8	5.7	5.0	2.8	1.3
Trucks and buses	0.8	0.9	1.1	1.4	1.6	1.5	1.7
Aircraft	0.01	0.01	0.03	0.05	0.06	0.08	0.09
Off-highway	0.8	0.9	0.9	0.9	0.9	1.1	1.1
Total	4.9	5.8	6.8	8.1	7.6	5.5	4.2
Particulates							
Autos	0.2	0.2	0.2	0.3	0.3	0.2	0.1
Trucks and buses	0.1	0.1	0.1	0.2	0.2	0.2	0.2
Aircraft	0.01	0.01	0.02	0.04	0.04	0.04	0.05
Off-highway	0.2	0.2	0.2	0.2	0.2	0.2	0.1
Total	0.5	0.5	0.5	0.7	0.7	0.6	0.5

Source: National Petroleum Council 1971.

TABLE 33

NATIONWIDE ESTIMATES OF VOLATILE
ORGANIC COMPOUNDS EMITTED FROM HIGHWAY VEHICLES*

	1970	1971	1972	1973	1974	1975	1976	1977
Highway emissions	10.6	10.6	10.9	10.7	10.0	9.8	10.0	9.9
Total of all transportation emissions	12.2	12.2	12.5	12.3	11.5	11.3	11.6	11.5

* Data in millions of tons per year.

Source: U.S. Environmental Protection Agency 1977c.

TABLE 34

SUMMARY OF TYPICAL EMISSION MODIFICATIONS

Model Year Added	Modification
1963	"Open" crankcase ventilation system a) Leaner mixture carburetor calibration b) Intake air pre-heat to constant temperature c) Intake manifold pre-heat d) Retarded idle timing e) "Closed" positive crankcase ventilation (PCV) system
1970	a) Decreased compression ratio b) Air injection (on some models) c) Modified spark advance control
1971	Fuel evaporative control system
1972	a) Anti-dieseling solenoid b) Fast acting choke c) Air injection
1973	a) Exhaust gas recirculation (EGR) b) Hardened valve seats c) Spark advance control
1974	a) Precision cams, bores, pistons b) Improved EGR systems

Source: Loftness 1978.

TABLE 35

PROPOSED AUTOMOBILE EMISSIONS STANDARDS

Emission standard (grams/mile)	Hydrocarbons			Carbon Monoxide			Nitrogen Oxides				
	1.5	0.9	0.41	15.0	9.0	3.4	3.1	2.0	1.5	1.0	0.4
Proposal (effective date)											
1970 Clean Air Act	1976		1977	1976		1977	1976	1977			1978
Schedule as of January 1976	1976-77		1978	1976-77		1978	1976	1977			1978
EPA proposal (March 5, 1976)	1977-79	1980-81	1982	1977-79	1980-81	1982		1977-81			
President's proposal (July 28, 1975)	1976-81			1976-81			1976-81				
Senate staff proposal (August 8, 1975)	1976-77		1978	1976-77		1978	1976-77			1978-81 ^a	1982
House subcommittee proposal	1976-77	1978-79	1980	1976-77	1978-79	1980		1977-79			1980 ^b
Senate committee bill	1976-78		1979	1976-78		1979	1976	1977-79		1979 ^c	
House committee bill	1976-79		1980	1976-79		1980	1976	1977-80			1981 ^d
1977 amendments	1976		1980	1976		1981	1976	1977			

^a Applies to only 50 percent of vehicles and engines in 1978 and 1979.

^b Administrator may grant annual suspensions based on unavailability of technology or excessive fuel penalties, but interim standards are not to exceed 1.5 gpm in 1980-81 and 1.0 gpm in 1982-84.

^c Applies to only 10 percent of vehicles in 1979 and 100 percent in 1980.

^d Administrator would be able to grant yearly suspension of this requirement. Maximum allowable standards with such suspension would be 2.0 for 1981-82, 1.5 for 1983-84 and 0.4 for 1985 and beyond.

Source: Council on Environmental Quality 1976, 1977.

Waste Lubricating Oils

Automotive, industrial, aviation, and other lubricating oils, when burned or used in various systems, end up as waste oils. It has been estimated that, on the average, 63 percent (i.e., $1,115 \times 10^6$ out of $2,234 \times 10^6$ gallons) of the oil sold in the U.S. in 1972 ended up as waste oil (U.S. Environmental Protection Agency 1974). In terms of ecological hazards, such a large volume of waste oil is of concern.

Waste automotive lubricants are the drained crankcase oils, transmission fluids, differential gear lubricants, hydraulic oils from automotive and construction equipment, and small quantities of solvents frequently used in servicing automobile equipment. Table 36 lists the synthetic organic additives containing sulfur, nitrogen, oxygen, and different metals that are used to reduce wear, resist oxidation, and inhibit corrosion, and that function as detergents, bactericides, and anhistalic agents. The organic portion of these additives is considered to be susceptible to losses due to combustion and reactions; however, the inorganics concentrate in the waste crankcase oil. The evaporative or volatile components are generally water and fuel. The soluble materials in the waste oil include viscosity index improvers and detergents, while insoluble materials include submicron sized carbon particles, dust, metal particles, and metal oxides, particularly lead oxides originating during fuel combustion. The metal content includes lead, calcium, zinc, phosphorus, barium, iron, vanadium, aluminum, copper, silicon, tin, sodium, and magnesium. Used automotive lubricating oils may also contain appreciable amounts of gasoline introduced through blow-by. Aluminum, copper, iron, lead, silicon, and tin are introduced by means of wear, combustion, and/or corrosion. Sodium, barium, calcium, zinc, and magnesium are added to lubricating oils by the oil manufacturer to impart specific properties to the oil. Use of catalytic converters and unleaded gasoline mandated by the Clean Air Act Amendments of 1970 reduce the lead and phosphorus content of waste lubricating oils.

It has been stated that virgin lubricating oil contains polynuclear aromatics which have been determined to be carcinogenic. Used oils show a higher percentage of such constituents than virgin oils (U.S. Environmental Protection Agency 1974). Used motor oils contain 13 percent monoaromatics, 3.52 percent diaromatics, and 62 percent polyaromatics (Whisman et al. 1975). Nitrosamines may also be found in used motor oils since both nitrogen and amine compounds are found in motor oils (Fin and Fan 1976).

The industrial lubricating oils used in metal industries are heavily contaminated with oxidized lubricating materials, sediment,

TABLE 36
COMPOSITION OF SOME LUBRICATING OIL ADDITIVES

Additive	Composition	Function
Corrosion inhibitor	Zn and Ba dithiophosphates, dithiocarbamates, metal sulfonates and sulfurized terpenes	To react with metal surfaces to form a corrosion-resistant film
Rust inhibitor	Sulfonates, alkylamines, amine phosphates, alkenylsuccinic acids, fatty acids, and acid phosphate esters	To react chemically with steel surfaces to form an impervious film
Antioxidant	Sulfides, phosphites, amines, phenols, dithiophosphates	To inhibit oxidation of oil
Detergent	Sulfonates, phosphonates, phenates, alkyl substituted salicylates combined with barium, magnesium, zinc, and calcium	To neutralize acids in crankcase oils to form compounds suspended in oil
Dispersant	Alkenyl succinimides, alkylacrylic polymers, ashless compounds	To disperse contaminants in the lubricant
Metal deactivator	Organic dihydroxphosphines, phosphates, and sulfur compounds	To form protective film on running surfaces to inhibit reaction
Color stabilizer	Amine compounds	To stabilize oil color
Viscosity index improver	Isobutylene polymers and acrylate copolymers	To retard loss of viscosity at high temperatures
Pour point depressant	Polymethacrylates, polyacrylamides, alkylated naphthalenes, and phenols	To prevent congealing of oil at low temperatures

TABLE 36 (Concluded)

Additive	Composition	Function
Extreme pressure additive	Organic compounds with sulfur, phosphorus, nitrogen, halogens, carboxyl or carboxalate salt	To form low-shear strength film providing lubrication at start-up and at high bearing loads
Antiodorant	Perfumes, formaldehyde compounds	To mask odors
Antiseptic	Alcohols, phenols, chlorine compounds	To inhibit microorganisms
Antiwear additive	Chlorinated waxes, organic phosphates, lead naphthenate	To form low-shear strength film providing lubrication
Tackiness agent	Polyacrylates and polybutenes	To improve adhesive qualities of base oil
Emulsifier	Surfactants, sulfonates, naphthenates and fatty acid soaps	To reduce interfacial tension and permit formation of water-oil emulsion

Sources: Swain 1977; Skinner 1976.

polychlorinated heat transfer and transformer oils, and finely divided, hard-to-filter particles. Other industrial waste oils consist of spent turbine oil, spent transformer oil, mixtures of aviation jet fuel and lubricants, gear box oils from industrial rotary machinery, heat transfer fluids, and railroad lubricants. There are indications that high levels of nitrosamines are present in metalworking fluids (Fin and Fan 1976). Waste metalworking oils may contain substantial amounts of iron, aluminum, copper, tin, and chromium, as well as fatty oils, soaps and emulsifiers, corrosion and rust inhibitors, sulfur, chlorine, and phosphorus compounds (Swain 1977).

The composition of waste oils from railroad service centers is similar to that reported for automotive waste oils, except that lead content is negligible and the flash point may average on the higher side.

Aviation service center waste oil includes jet fuel drain from aircraft, aircraft sumping, loading facility spills, draining of petroleum based engine and transmission lubricants, synthetic lubricants from the aircraft exterior, and ground support equipment washing and deicing fluids (e.g., ethyl glycol). A significant quantity of waste oils and other compounds appear in aircraft wastewater and storm water sewers. Also included among waste oils are paint strippers, solvents, degreasers, washdown waters, and plating wastes.

Control of Emissions

Atmospheric emissions of nitrogen oxides, carbon monoxide, sulfur oxides, hydrocarbons, and particulate matter from stationary and mobile source combustion are effectively controlled or reduced with the proper use of engineering controls that are either retrofitted or built into the combustion process equipment. These control measures are identified in the discussion below.

Stationary Source

Reduction of air polluting emissions by process, operational, and system control is not only an important adjunct to air and gas cleaning technology and to atmospheric dispersion, but it also is a definitive response to the concept of zero emissions when it can be employed for total control. In general, filtration, electrostatic precipitation, scrubbing, mist elimination, and adsorption are some of the techniques used to control hazardous emissions.

The quantity of sulfur oxides emitted depends on the amount of sulfur present in oil and natural gas that is burned. SO_x emissions generally are low and are significantly less when compared with

those from coal-fired boilers. Raw natural gas may contain a significant quantity of hydrogen sulfide, but it is generally removed from the gas before distribution and widespread utilization. Thus, the combustion of natural gas emits only low levels of sulfur oxides.

About 90 to 95 percent of nitrogen oxides are emitted as nitric oxide and the remainder is nitrogen dioxide. Carbon monoxide and gaseous hydrocarbons are emitted as a result of incomplete combustion of the oil and gas. In properly designed and operated units, the quantities of carbon monoxide are less than 100 ppm for gas-fired furnaces and 20 ppm for oil-fired furnaces. However, in poorly designed and operated systems, emissions may be increased by 10 or 100 times (Engdahl and Barrett 1977). Table 37 summarizes the different control measures used to reduce atmospheric emissions from stationary source combustion of oil and gas. In California these techniques have reduced NO_x emissions from utility boilers sufficiently to meet emissions standards of 160 ppm for gas-fired and 250 ppm for oil-fired utility boilers.

Mobile Source

Automobile emissions control, achieved through changes in equipment design or legal constraints, is a compromise involving the superposition of emissions regulations upon an engine that was developed over a period of 60 years with practically no consideration of the composition of the exhaust. Pre-1977 engine design objectives of low cost, high power-to-weight ratio, high power-to-size ratio, good durability, low maintenance, high reliability, and low fuel consumption have put constraints on the additional design objectives of reducing pollutant emissions. Table 37 also summarizes various means and control techniques used to reduce emissions from mobile sources.

The retrofit of emissions controls on in-use vehicles has been successfully accomplished, most notably in California, a state that required installation of retrofit emission controls on 1955 through 1970 model vehicles upon change of ownership. These devices were intended to control exhaust hydrocarbons and nitrogen oxides. Carbon monoxide emissions also were controlled by retrofit devices for 1966 to 1970 models. The U.S. Environmental Protection Agency has specified various retrofit strategies to reduce vehicle pollution in localities with special problems. Installation of emission controls in new motor vehicles after they leave the assembly line has been successful in special situations. This was accomplished, for example, with the Russian-built Lada vehicle when it was prepared for export to the U.S. and other countries (Olson 1977).

Aircraft emissions can be controlled through engine modifications without degrading engine reliability or seriously reducing

TABLE 37

EMISSION CONTROL TECHNIQUES

Combustion Source	Control Techniques
<u>Stationary sources</u>	
Utility boilers	Biased firing and flue-gas recirculation. Firing with very low excess air.
Commercial and industrial boilers	Improve burner design, flue-gas recirculation, staged combustion, flue additives, and oil/water emulsions.
Residential boilers	Adjustment of excess air level and well tuned furnaces.
Steam electric power plants	Tangentially fired units, over-fire air simulation, and flue-gas recirculation.
Gas turbine and diesel operated power plants	Timing retardation and staged injection in engines.
<u>Mobile sources</u>	
Automotive engines (internal combustion)	
Total emissions	Variations in engine design, engine types, engine efficiency, combustion processes and fuel factors.
Blow-by emissions	Routing blowing to the engine induction system or use of closed positive ventilating system.
Evaporative emissions	Use of an activated carbon canister for absorption and temporary storage of evaporative hydrocarbons.

TABLE 37 (Continued)

Combustion Source	Control Techniques
Exhaust emissions	<p>Exhaust treatment through the use of thermal reactors, catalytic reactors, and particulate traps.</p> <p>Adjustment of the air/fuel mixture through the use of carburetors, fuel injection systems, feed back systems, exhaust gas recirculation, and fuel modification.</p> <p>Combustion chamber modifications, including spark timing retardation, compression ratio reduction, combustion chamber geometry modification, and high energy ignition systems.</p> <p>Any combination of the three techniques listed above.</p>
Stratified-charge engines	Variations such as torch-ignition (with pre-chambers), divided chamber, and open chamber.
Diesel engines	Control technique currently under research and development.
Locomotives and ships (diesel powered)	Improved diesel fuel injectors, variation in injection timing, humidification of inlet air, reduction of scavenging efficiency, and exhaust gas recirculation.
<u>Turbine engines</u>	
Existing engines	<p>Minor modification of combustion chamber and fuel nozzle to achieve best state-of-the-art emission performance.</p> <p>Major modification of combustion chamber and fuel nozzle, incorporating advanced fuel injection concepts (carburetion or pre-vaporization).</p>

TABLE 37 (Continued)

Combustion Source	Control Techniques
	<p>Modify fuel supply system or fuel drainage system to eliminate release of drained fuel to environment.</p> <p>Provide independent fuel supplies to subsets of fuel nozzles to allow shutdown of one or more subsets during low-power operation.</p> <p>Install water injection system for short duration use during maximum power (takeoff and climb-out) operation.</p> <p>Increase air bleed rate from compressor at low-power operation to increase combustor fuel-air ratio.</p>
<u>Future engines</u>	
Variable geometry	Use of variable airflow distribution to provide independent control of combustion zone fuel-air ratio.
Staged injection combustor	Use of advanced combustor design concept involving a series of combustion zones with independently controlled fuel injection in each zone.
<u>Piston engines</u>	
Existing engines	<p>Limiting rich fuel-to-air ratios to only those necessary for operational reliability.</p> <p>Inject air at a controlled rate into each engine exhaust port.</p> <p>Install air injection thermal reactor in place of or downstream from an exhaust manifold.</p>

TABLE 37 (Concluded)

Combustion Source	Control Techniques
Existing engines (continued)	<p data-bbox="773 420 1350 544">Install thermal reactor with injection of air and additional fuel in exhaust system (direct-flame afterburner).</p> <p data-bbox="773 565 1350 731">Inject water into intake manifold with simultaneous reduction in fuel rate to provide for cooler engine operation at leaner fuel-to-air ratios.</p> <p data-bbox="773 752 1350 959">Use positive crankcase ventilation. The PCV system now used with automotive engines can be applied to aircraft engines. This would be effective only in combination with one of the control methods listed above.</p> <p data-bbox="773 980 1350 1270">Use evaporative emission controls--a group of control methods used singly or in combination to reduce evaporative losses from the fuel system. Control methods commonly used include charcoal absorbers and vapor traps in combination with relatively complex valving and fuel flow systems.</p>
Future engines	<p data-bbox="773 1311 1350 1560">Coordinated redesign of combustion chamber geometry, compression ratio, fuel distribution system, spark and valve timing, fuel-to-air ratio, and cylinder wall temperature to minimize emissions while maintaining operational reliability.</p>

Source: Olson 1977.

performance. These emissions modifications have been previously discussed (Olson 1977).

Control of carbon monoxide emissions and total hydrocarbons at carrier airports can be accomplished by modifying ground-operation procedures for turbine aircraft. The control methods include: increasing engine speed while reducing the number of engines operating during idling and taxiing, reducing operating time by controlling departure times from gates, reducing taxiing time by transporting passengers to aircraft and by towing aircraft between runway and gate, and reducing operation of the aircraft auxiliary power supply by providing a ground-based power supply. These control methods may be difficult to implement at busy general aviation airports and international airports such as the Kennedy Airport in New York, O'Hare Airport in Chicago, Orly Airport in Paris, and Heathrow in London.

Oxidants

Photochemical oxidants, called ozone, or PAHs, are rarely emitted directly by sources. Instead, they are secondary pollutants, so control can be achieved only by directing efforts toward controlling precursors, or primary pollutants that contribute to the formation of photochemical oxidants. These precursors are organic compounds, mainly hydrocarbons and nitrogen oxides, predominantly emitted from motor vehicles and stationary combustion sources. The ratio of hydrocarbons to NO_x is critical in order to achieve a substantial reduction in the ozone level of 0.25 ppm (a common near-maximum for regions other than Los Angeles). Table 38 presents the results derived from an ozone isopleths* model used to calculate the non-methane hydrocarbon (NMHC) and/or NO_x control requirements needed to reduce 0.25 ppm ozone to 0.16, 0.12, or 0.08 as a function of the NMHC-to- NO_x ratio. Based on this model, the conclusions derived by the Air Management group of the Organization for Economic Cooperation and Development (OECD) are listed below (1979):

- o Only when the NMHC-to- NO_x ratio is below 10 is there an 80 percent reduction in hydrocarbon levels (predicted to reduce 0.25 ppm ozone to less than 0.08 ppm). In all cases greater than 80 percent, control of nitrogen oxides emissions is required to meet this objective.

*The ozone isopleths model uses relationships among SO_x , HC, and NO_x , derived from smog chamber data.

TABLE 38

HYDROCARBON AND/OR NITROGEN OXIDE CONTROL REQUIREMENTS^a

Reduce 0.25 ppm Ozone to:	Reduction of NMHC (percent)	Reduction of NO _x (percent)	Reduction of Both NMHC and NO _x (percent)
<u>NMHC:NO_x = 5</u>			
0.16	43	71	No advantage ^b
0.12	51	88	No advantage ^b
0.08	66	93	No advantage ^b
<u>NMHC:NO_x = 10</u>			
0.16	63	63	50 each
0.12	69	83	62 each
0.08	82	89	80 each
<u>NMHC:NO_x = 20</u>			
0.16	73	57	49 each
0.12	80	79	67 each
0.08	90	85	81 each
<u>NMHC:NO_x = 30</u>			
0.16	78	54	Little advantage ^c
0.12	84	74	Little advantage ^c
0.08	92	82	Little advantage ^c

^aControl requirements to reduce 0.25 ppm ozone to 0.16, 0.12, or 0.08 as a function to NMHC-to-NO_x ratio.

^bNo advantage over unilateral HC control

^cLittle advantage over unilateral NO control.

Source: Organization for Economic Cooperation and Development 1979.

- o Technical limitations, deterioration in performance of control devices; and accidental, fugitive, natural, and uncontrollable emissions of precursors are constraints that limit hydrocarbon reductions and make it almost impossible to reduce the NO_x level by the desired amount.
- o It is advantageous to control both precursors and achieve ratios between 10 and 20, particularly when less strict air quality goals are to be met.

Different control measures introduced to reduce emissions of hydrocarbons and nitrogen oxides from stationary and mobile sources were discussed earlier. Changes in emissions standards for NO_x and hydrocarbons caused reductions in the emissions of precursors of photochemical oxidants.

Lead

Among the lead particles emitted from gasoline combustion, 40 to 75 percent are less than 1 um in diameter. Hence, these emissions are difficult to control with particulate control equipment.

Methods of control include reducing the lead level in gasoline from 1.7 gm per gallon prior to 1979 to 0.5 gm per gallon as of Oct. 1, 1979, and using lead particulate traps. The first method is expected to reduce lead emissions associated with combustion by approximately 65 percent and the second by more than 90 percent. Lead emissions from waste oil disposal can be controlled by preheating before burning, blending with fuel oil, and/or reducing lead in gasoline. These methods will reduce lead emissions from waste oil and gasoline by 65 percent. Fugitive lead emissions from boiler and furnace leaks can be controlled by proper maintenance of the equipment such as by sealing furnaces and ductwork.

Total lead emissions from automobiles are estimated to be reduced from 140,900 tons in 1975 to 49,500 tons in 1985, assuming a 2 percent annual increase in average consumption. The lead emissions from waste oil disposal are estimated to be reduced from 5,480 tons in 1975 to 2,300 in 1985 (U.S. Environmental Protection Agency 1977b).

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HEALTH EFFECTS OF OIL AND GAS USE

In previous sections, emissions estimates and measurements from stationary and mobile source combustion were presented. Following control, the magnitude of these emissions may be sizable and may pose a health hazard through chronic, low-level exposure. Table 39 shows the nationwide air pollution emissions by pollutant and source from 1968 to 1974. Table 40 summarizes the major air pollutants and their principal health and environmental effects (Council on Environmental Quality 1975). These effects are discussed in this section along with research problems germane to the use of oil and gas.

Outdoor Air Pollution

A concern is the occasional discomfort and long-term alterations in physiological functions experienced by the general population and occupational groups as a result of exposure to levels of air pollutants elevated above national ambient levels. In terms of emissions per unit of energy released, more inorganic substances (NO_x , SO_x , and CO) are generated from coal, while more hydrocarbons are released from oil. Except for NO_x , natural gas is relatively non-polluting when compared to coal and oil. The data below reflect the relative pollutant emission rates of electric power plants using coal, oil, or natural gas as an energy source (Gartrell 1977).

Pollutant	Relative Emission Rates		
	Coal (lbs/Btu)	Oil (lbs/Btu)	Gas (lbs/Btu)
NO_x	0.80	0.69	0.37
SO_2	3.04 ^a	2.09 ^a	0.0004
SO_3	0.048 ^a	0.033 ^a	b
CO	0.02	0.0003	b
HC as methane	0.008	0.021	b
Aldehyde as formaldehyde	0.0002	0.004	0.0009
Particulate matter	0.204	0.002	0.014

^aAssumes the use of coal with a 2 percent sulfur content.

^bData unavailable.

TABLE 39
NATIONWIDE AIR POLLUTION EMISSIONS
BY POLLUTANT AND SOURCE

Pollutants and Sources	Emissions (millions of tons per year)			
	1968	1970	1972	1974
Particulates				
Transportation ^a	1.2	1.2	1.3	1.3
Stationary combustion sources ^b	8.9	8.3	7.1	5.9
Others ^c	18.2	18.0	14.8	12.3
Total	28.3	27.5	23.2	19.5
Sulfur oxide				
Transportation	0.8	0.7	0.7	0.7
Stationary combustion sources	24.4	27.0	25.2	24.3
Others	8.0	6.0	6.2	6.3
Total	33.2	34.3	32.6	31.4
Carbon monoxide				
Transportation	63.8	82.3	83.4	73.5
Stationary combustion sources	1.9	1.1	1.0	0.9
Others	34.4	23.9	20.5	20.2
Total	100.1	107.3	104.9	94.6
Hydrocarbons				
Transportation	16.6	14.7	14.1	12.8
Stationary combustion sources	0.7	1.6	1.7	1.7
Others	14.7	15.8	13.5	15.9
Total	32.0	32.1	31.3	30.4
Nitrogen oxides				
Transportation	8.1	9.3	10.5	10.7
Stationary combustion sources	10.0	10.1	10.8	11.0
Others	2.5	1.0	0.9	0.8
Total	20.6	20.4	22.2	22.5

^aIncludes automobiles, aircraft, railroads, vessels, and nonhighway motor fuel use.

^bIncludes coal, fuel oil, and natural gas.

^cIncludes industrial processes and solid waste disposal.

Source: Adapted from Loftness 1978.

TABLE 40

MAJOR AIR POLLUTANTS AND THEIR PRINCIPAL EFFECTS^a

Pollutant	Characteristics	Principal Sources	Principal Effects	Controls	National Ambient Standards ^b (in micrograms per cubic meter)	
Total suspended particulates (TSP)	Any solid or liquid particles dispersed in the atmosphere, such as dust, pollen, ash, soot, metals, and various chemicals; the particles are often classified according to size as settleable particles, larger than 50 microns; aerosols, smaller than 50 microns; and fine particulates, smaller than 3 microns.	Natural events such as forest fires, wind erosion, volcanic eruptions; stationary combustion, especially of solid fuels; construction activities; industrial processes; atmospheric chemical reactions.	Health: Directly toxic effects or aggravation of the effects of gaseous pollutants; aggravation of asthma or other respiratory or cardio-respiratory symptoms; increased cough and chest discomfort; increased mortality. Other: Soiling and deterioration of building materials and other surfaces, impairment of visibility, cloud formation, interference with plant photosynthesis.	Cleaning of flue gases with inertial separators, fabric filters, scrubbers, or electrostatic precipitators; alternative means for solid waste reduction; improved control procedures for construction and industrial processes.	Primary:	Annual = 75 24-hour = 260
					Secondary:	Annual = 60 24-hour = 150
					Alert:	24-hour = 375
Sulfur dioxide (SO ₂)	A colorless gas with a pungent odor; SO ₂ can oxidize to form sulfur trioxide (SO ₃), which forms sulfuric acid with water.	Combustion of sulfur-containing fossil fuels, smelting of sulfur-bearing metal ores, industrial processes, natural events such as volcanic eruptions.	Health: Aggravation of respiratory diseases, including asthma, chronic bronchitis, and emphysema; reduced lung function; irritation of eyes and respiratory tract; increased mortality. Other: Corrosion of metals; deterioration of electrical contacts, paper, textiles, leather, finishes and coatings, and building stone; formation of acid rain; leaf injury and reduced plant growth.	Use of low-sulfur fuels; removal of sulfur from fuels before use; scrubbing of flue gases with lime or catalytic conversion.	Primary:	Annual = 80 24-hour = 365
					Alert:	24-hour = 800
Carbon monoxide (CO)	A colorless, odorless gas with a strong chemical affinity for hemoglobin in blood.	Incomplete combustion of fuels and other carbon-containing substances, such as in motor vehicle exhausts; natural events such as forest fires or decomposition of organic matter.	Health: Reduced tolerance for exercise, impairment of mental function, impairment of fetal development, aggravation of cardiovascular diseases. Other: Unknown.	Automobile engine modifications (proper tuning, exhaust gas, recirculation, redesign of combustion chamber); control of automobile exhaust gases (catalytic or thermal devices); improved design, operation, and maintenance of stationary furnaces (use of timely dispersed fuels, proper mixing with air, high combustion temperature).	Primary:	8-hour = 10,000 1-hour = 40,000
					Alert:	8-hour = 17,000

TABLE 40 (Concluded)

Pollutant	Characteristics	Principal Sources	Principal Effects	Controls	National Ambient Standards ^b (in micrograms per cubic meter)
Photochemical oxidants (O_x)	Colorless, gaseous compounds which can comprise photochemical smog, e.g., ozone (O_3), peroxyacetyl nitrate (PAN), aldehydes, and other compounds.	Atmospheric reactions of chemical precursors under the influence of sunlight.	Health: Aggravation of respiratory and cardiovascular illness, irritation of eyes and respiratory tract, impairment of cardiopulmonary function. Other: Deterioration of rubber, textiles, and paints; impairment of visibility; leaf injury, reduced plant growth, and premature fruit and leaf drop in plants.	Reduced emissions of nitrogen oxides, hydrocarbons, possibly sulfur oxides.	Primary: 1-hour = 160 Alert: 1-hour = 200
Nitrogen dioxide (NO_2)	A brownish-red gas with a pungent odor, often formed from oxidation of nitric oxide (NO).	Motor vehicle exhausts, high temperature stationary combustion, atmospheric reactions.	Health: Aggravation of respiratory and cardiovascular illnesses and chronic nephritis. Other: Fading of paints and dyes, impairment of visibility, reduced growth, and premature leaf drop in plants.	Catalytic control of automobile exhaust gases, modification of automobile engines to reduce combustion temperature, scrubbing flue gases with caustic substances or urea.	Primary: Annual = 100 24-hour = 282 1-hour = 1,130
Hydrocarbons (HC)	Organic compounds in gaseous or particulate form, e.g., methane, ethylene, and acetylene.	Incomplete combustion of fuels and other carbon-containing substances, such as in motor vehicle exhausts; processing, distribution, and use of petroleum compounds such as gasoline and organic solvents; natural events such as forest fires and plant metabolism; atmospheric reactions.	Health: Suspected contribution to cancer. Other: Major precursors in the formation of photochemical oxidants through atmospheric reactions.	Automobile engine modifications (proper tuning, crankcase ventilation, exhaust gas recirculation, redesign of combustion chamber); control of automobile exhaust gases (catalytic or thermal devices); improved design, operation, and maintenance of stationary furnaces (use of finely dispersed fuels, proper mixing with air, high combustion temperature); improved control procedures in processing and handling petroleum compounds.	Primary: 3-hour = 160

^aPollutants for which national ambient air quality standards have been established.

^bPrimary standards are intended to protect against adverse effects on human health. Secondary standards are intended to protect against adverse effects on materials, vegetation, and other environmental values. The federal episode criteria specify that meteorological conditions are such that pollutant concentrations may be expected to remain at these levels for 12 or more hours or to increase; in the case of oxidants, the situation is likely to reoccur within the next 24 hours unless control actions are taken.

Source: Council on Environmental Quality 1975.

Projections of electricity generation for 1980 to 2000 suggest that coal use for power generation will increase from 1.1 kWh per year in 1980 to 2 kWh per year in 2000, while oil and gas consumption for power generation will remain at 0.5 kWh per year for oil and 0.3 kWh per year for gas (Gartrell 1977). From past projections, it is evident that a much smaller quantity of pollutants such as sulfur dioxide, sulfur trioxide, and particulates will be generated from oil and gas than from coal. The data do not reflect the uncertainties associated with implementation of the Energy Security Act of 1980, especially with respect to oil and gas in the form of synthetic fuels. The mobile source emissions of hydrocarbons, carbon monoxide, and nitrogen oxides contribute significantly to the nationwide air pollutant emissions as seen in Table 39. Hydrocarbon emissions from transportation constitute about 40 to 45 percent of total hydrocarbon emissions, while nitrogen oxides from transportation account for 40 to 48 percent of total NO_x emissions in the U.S. Carbon monoxide emissions from transportation comprised approximately 76 percent of the total CO emissions in the U.S. during the period reflected by the data.

The effects of these air pollutants on human health may include: acute sickness or death; insidious or chronic disease, shortening of life, or impairment of growth or development; alteration of important physiological functions (e.g., ventilation of the lung, transport of oxygen by hemoglobin, sensor acuity, time interval estimation, or other functions of the nervous system); impairment of performance; sensory irritation such as discomfort, odor, and impairment of visibility; and bioaccumulation of potentially hazardous materials in the body. In the following paragraphs particular health effects associated with major oil and gas pollutants such as nitrogen oxides, hydrocarbons, carbon monoxide, photochemical smog, and ozone are discussed.

Nitrogen Oxides

The effects of nitrogen oxides on health have been extensively studied in experimental animals as well as in human clinical and epidemiological studies, and are reported in a Federal criteria document (National Institute for Occupational Safety and Health 1976). Comparative toxicity data taken from the document show a direct dose-response relationship:

Pollutant	Dose	Effect
NO ₂	1,500 ppm and more	100% death
	1,200 ppm	100% survival
NO	3,500 ppm	100% death in 4 to 5 minutes
	350 ppm	100% death
	320 ppm	50% death
	310 ppm	10% survival following 8-hr exposure

It is apparent that nitric oxide is approximately four times more toxic than nitrogen dioxide. Carcinogenic effects of nitrogen oxides are not conclusive and further work is needed. Evidence of mutagenesis by nitrogen dioxide or its derivatives in animal species has not been found in the literature. However, nitrous acid, which is one of the products of the reaction of nitrogen dioxide with water at normal temperatures, has been shown to have potent mutagenic effects on lower forms of life such as the tobacco mosaic virus and Escherichia coli.

The effects of nitrogen oxides on humans listed below are summarized in the criteria document (National Institute for Occupational Safety and Health 1976).

- o Initial local irritation; reversible symptoms of breathlessness, cyanosis, vomiting, giddiness, stupefaction, delirium, fainting, cough, mild fever, and unconsciousness;
- o Milder respiratory and gastrointestinal symptoms;
- o Shock-like illness such as instantaneous asphyxia, convulsions and respiratory arrest;
- o Severe methemoglobinemia; and
- o Acute and potentially lethal pulmonary edema and/or bronchitis fibrosa obliterus.

Animal experiments and human studies suggest that the principal direct action of nitric oxide upon humans is the conversion of hemoglobin to methemoglobin (one of the inactive forms of hemoglobin). Nitric oxide poisoning effects are solely due to the hypoxemia which

is secondary to the methemoglobinemia. No quantitative exposure effect relationship can be made for nitric oxide due to the lack of any measured environmental data on human exposure. Animal studies show a dose-response relationship.

The acute and usually delayed effects of high concentrations of nitrogen dioxide on man are well established. These include an irritant cough, a slight headache, and mild dyspnea before the onset of acute and potentially lethal pulmonary edema. The critical concentration of NO_2 needed to produce acute pulmonary edema or bronchitis fibrosa obliterations is not known. These conditions have even been reported for low, but relatively steady levels of exposure associated with the few industrial processes in which oxides of nitrogen are steadily generated and continuously permitted to enter the workplace atmosphere.

Generally, subacute and chronic responses to low levels of nitrogen dioxide are not well defined for humans. Research has not definitely established that methemoglobinemia occurs in man from exposure to NO_2 . Acute effects of low levels of NO_2 in man include a decrease in effective lung compliance, alteration of pulmonary mechanics, and increased airway resistance in chronic bronchitis patients. It is not known whether any or all of these effects are completely reversible following repeated intermittent exposures over an extended period. There has been much speculation as to whether chronic low-level exposure to NO_2 , among other irritant gaseous air pollutants, may be a contributory cause of chronic obstructive pulmonary disease in man. A variety of other effects of nitrogen dioxide exposures, including changes in pulmonary physiology, biochemical changes in the lung, pulmonary surfactant, enzymetric changes in remote organs, changes in macrophage populations and behavior, and immunological changes, have been observed.

Determining whether nitrogen oxides are carcinogenic or mutagenic will require new data. The possibility exists that nitrogen dioxide may act as a co-carcinogen or carcinogenic "promoter;" however, data are insufficient.

Nitrosamines. Oxides of nitrogen have the intrinsic chemical property of reacting with primary and secondary amines present in the body tissues, food, tobacco, water, and in workplace air to form nitrosamines. Effects of nitrosamine exposure in experimental animals are listed below (National Institute for Occupational Safety and Health 1976).

Route of Exposure	Effects of N-nitroso Compounds
Inhalation	Acutely toxic; polydypsia; loss of appetite; ascites hyperactive liver necrosis; leukopenia; and disruption of normal blood coagulation; hemorrhage into the walls of the gastrointestinal tract, the abdominal cavity, and other tissues.
Inhalation of relatively high concentrations for a short period	Liver damage; severe hematologic changes; and carcinoma of the nasal cavity, trachea, and lungs.

No animal data or human epidemiological data have been found indicating chronic effects of long-term exposure to airborne secondary nitrosamines. Further research is needed to establish the potential hazards of nitrosamines for humans.

Occupational Exposure. Under normal, well-maintained conditions, utility, industrial, commercial, and residential boilers and furnaces are unlikely to cause workers and residents to be exposed to nitrogen oxides emissions. Exposure to nitrogen oxides fumes is possible only during accidental leaks, explosions, bursts, and process upsets. Sufficient general ventilation in boiler rooms reduces the impact of such hazards.

Control of nitrogen oxides from indoor vehicular operation is usually dependent upon providing sufficient ventilation. Where work is performed on stationary vehicles (as in repair garages), the room's exhaust system should be attached to or located close to the vehicle tailpipes. This would limit exposure not only to nitrogen dioxide, but also to other contaminants, particularly carbon monoxide. Similar control measures can be applied to gas and diesel engines operated in enclosed areas such as mines and tunnels.

Ambient Exposure. The current Federal standard* for nitrogen dioxide is 5 ppm as an 8-hour time weighted average (TWA) and the one

*Standard for nitrogen dioxide and nitric oxide established as announcement 29CFR1910.1000 published in the Federal Register 39: 23542, June 27, 1974.

for nitric oxide is 25 ppm as an 8-hour TWA. Following a 1976 review of current regulations, scientists concluded that the Federal standard of 5 ppm should be reduced to a ceiling of 1 ppm to prevent acute irritation of the lungs of workers exposed to NO₂ (National Institute for Occupational Safety and Health 1976). They also recommended that, in the absence of conclusive data, the current Federal standard of 25 ppm as an 8-hour TWA should be continued for up to 10 hours per day and 40 hours per week to protect workers from exposure to nitric oxide. Future research may determine the nitric oxide concentrations that impair respiratory or other biological functions so a secondary standard may be promulgated.

Many workers are exposed to nitrogen oxides at ambient air concentrations or at concentrations considerably below recommended occupational limits. However, concern for worker health requires that protective measures be instituted below the enforceable limits to ensure that exposures do not exceed standards. Thus, a working definition of occupational exposure to nitrogen oxides is: "exposure above half the environmental limits, thereby delineating those work situations which do not require the installation of unnecessary controls and the expenditure of health resources for provisions such as environmental and medical monitoring and associated recordkeeping" (National Institute for Occupational Safety and Health 1976).

Hydrocarbons

Evaporative hydrocarbons contribute to photochemical oxidant formation in the atmosphere, indirectly affecting human health, and also act as irritants or simple asphyxiants. The largest constituents of particulate hydrocarbons are polynuclear aromatic hydrocarbons, and exposure to these results in respiratory tract diseases including cancer. Diesel exhaust emissions, which contain hydrocarbons, are considered below in a special section. The prospect that passenger cars equipped with diesel engines will soon represent a significant portion of new car production raises an important question concerning their possible impact on human health.

Volatile Hydrocarbons. Volatile hydrocarbons emitted from various sources and those identified in ambient air are listed in Table 41. Evaporative hydrocarbons include aliphatic, alicyclic, and aromatic compounds. Based on data available prior to 1970 when the Air Quality Criteria for Hydrocarbons was published, it was concluded that no obvious health effects directly relate to ambient concentrations of gaseous or volatile hydrocarbons as a pollutant class (U.S. Department of Health, Education, and Welfare 1970). This document was instrumental in developing a nonmethane hydrocarbon air quality standard of 160 ug per m³ (0.24 ppm) over 3 hours that is not to be exceeded more than once per year.

TABLE 41
VOLATILE HYDROCARBONS IDENTIFIED IN VARIOUS COMBUSTION SOURCES

Combustion Sources ^a	Stationary External Combustion Sources ^a	Stationary Internal Combustion Sources ^a	Utility Boilers and Turbines ^b	Gasoline Auto Exhaust ^c	Diesel Auto Exhaust ^d	Ambient Air Volatile Hydrocarbons ^e (partial listing)
Aliphatic	Methane Ethane Propane n-Butane Isobutane n-Pentane Isomer of pentane n-Hexane Isomer of hexane n-Heptane Isomer of heptane n-Octane Isomer of octane Ethylene Acetylene Propylene	Methane Ethane Propane n-Butane Isobutane Ethylene Acetylene Propylene Butene 1,3-Butadiene	Methane Ethane Propane n-Butane Isobutane n-Pentane 1-Pentane Hexane Heptane Octane Isomer of hexane Isomer of heptane Isomer of octane Isomer of nonane Isomer of decane Isomer of pentane Ethylene Acetylene Propylene	Methane Ethane n-Butane Isopentane n-Pentane 1-Butene n-Hexane Isoctane 2-Methylpentane Ethylene Acetylene Propylene	Methane Ethane Propane 1-Butane 2-Butene Isobutylene 1,3-Butadiene Ethylene Acetylene Propylene	Methane Ethane Propane Butane Isobutane Pentane Isomer of pentane Hexane Heptane Octane Nonane Decane Undecane Dodecane Hexadecane Acetylene Ethene Propylene 1-Butene Isomer of butene
Alicyclic	Cyclohexane		Cyclohexane Cycloparaffins			Cyclopentane, cyclopentene, cyclohexane
Aromatic	Benzene	Benzene	Benzene Toluene	Benzene Toluene, m- and p-xylene	Benzene	Benzene, toluene, o-, m-, and p-xylene, ethylbenzene, styrene, cumene
Aldehydes	Formaldehyde	Formaldehyde	Formaldehyde	Formaldehyde	Formaldehyde Acetaldehyde Crotonaldehyde Hexanaldehyde Benzaldehyde Acrolein	
Ketones			Acetone	Acetone	Acetone	

^aSource: Bucon et al. 1970; EPA-450/3-78-119.

^bSource: Taback et al. 1978.

^cSource: National Academy of Sciences 1976b.

^dSource: Braddock and Gabel 1977.

^eSource: Graedel 1978.

Since promulgation of the hydrocarbon standards in 1971, the effects of hydrocarbons on public health have been extensively studied. A review by the author of the literature since 1970 indicates that evaporative hydrocarbons do not present a significant health hazard in the atmosphere at the average nationwide levels. Higher levels near refineries, petrochemical facilities, and storage and handling facilities may represent local health hazards. All of these hydrocarbons should be controlled or restricted to minimize their contribution to photochemical oxidants, namely smog, ozone, and peroxysoyl nitrates.

Toxicological and clinical studies on aliphatic (saturated and unsaturated), alicyclic, and aromatic hydrocarbons that provide the basis for assessing health effects are well summarized elsewhere (Gerarde 1963a, b, c). Aliphatic hydrocarbons are toxicologically inactive at concentrations many times above those generally found in the atmosphere. No obvious effects are observed at levels below 500 ppm for the alkanes and 1,000 ppm for the alkenes. These aliphatic hydrocarbons, when present in high concentrations in the air, act as simple asphyxiants without other significant physiological effects. Any systemic effects that may be observed are thought to be secondary due to the oxygen-replacing capabilities of these gaseous and/or vapor phase hydrocarbons at extremely high concentrations. Generally, alkanes as a group show increasingly strong narcotic properties.

Exposure to only one alkane is infrequent, so the National Institute for Occupational Safety and Health (NIOSH) (1977) has recommended a TWA concentration level of 350 mg per m³ as the occupational limit for pentane, hexane, laptane, octane, and alkane mixtures. This recommended standard is based on the conclusion that acute intoxication by these alkanes involves a transient central nervous system depression and that chronic intoxication may involve a more persistent effect, polyneuropathy. No strong evidence suggests that any volatile aliphatic hydrocarbon has carcinogenic, mutagenic, or teratogenic effects on humans or experimental animals. On the basis of limited bioassay data, alkanes and alkenes are not considered to be carcinogens.

Like aliphatics, alicyclic hydrocarbons act as general anesthetics and central nervous system depressants. They are generally biochemically inert and are only reactive at concentrations 100 to 1,000 times higher than average levels found in the atmosphere. Alicyclic hydrocarbons (naphthenes), which are present in relatively low concentrations in modern gasoline and gasoline vapors, have not been indicated as hematopoietic toxicants. These compounds are rapidly metabolized and eliminated in the urine, thus eliminating the

chance of increased body burden upon repeated exposure to low atmospheric concentrations. No occupational or epidemiological evidence is available which indicates that naphthenes have any systemic effect. Naphthene vapors at very high concentrations cause irritation of mucous membranes. No available studies indicate a definite human carcinogenic, mutagenic, or teratogenic potential of any alicyclic hydrocarbon.

The primary route of exposure to the levels and kinds of aromatic hydrocarbons that are biochemically and biologically active is by vapor inhalation. Systemic injury can result from the inhalation of aromatic hydrocarbon vapors above a concentration of 22 ppm. Acute poisoning by high concentrations of benzene, toluene, and xylene can produce effects on the central nervous system that are usually reversible. The symptoms of acute narcosis include drowsiness, vertigo, nausea, unconsciousness, and death.

The health effects of benzene have been extensively studied. Benzene exposure by inhalation and other routes is strongly implicated in leukemia, pancytopenia, and chromosomal aberrations. The more severe long-term hazard is to the hematopoietic system and affected blood parameters include erythrocyte count, hemoglobin, mean corpuscular volume of red blood cells, platelet counts, and leukocyte counts. The carcinogenic potential of benzene has been suggested primarily through the experience of human occupational exposure. In recognition of accumulated clinical and epidemiological evidence that benzene causes leukemia and probably other severe illnesses, a much more stringent standard for occupational exposure to benzene has been recommended. The proposed occupational standard, setting a maximum of 1 ppm benzene for 60 minutes, was expected to materially reduce the risk of benzene-induced leukemia from that incurred at the present acceptable ceiling of 25 ppm. Recently, however, the U.S. Supreme Court blocked enforcement of the lower benzene exposure limit.

Other aromatic hydrocarbons such as toluene and xylene are considered to be less toxic and volatile than benzene. Organ-specific effects due to toluene exposure involve organs other than hematopoietic systems--the nervous system, liver, kidney, heart, mucous membrane, immune system, and the skin. The reported effects for some of these organs are inconsistent and need further verification. A recommended Federal standard for occupational exposure to toluene is determined as 100 ppm TWA for an 8-hour day, with a ceiling concentration of 200 ppm (National Institute for Occupational Safety and Health 1973). The only well documented effects that a xylene standard should protect against are the irritating and narcotizing properties of xylene. Recently, xylenes have been shown to produce necrosis of living tissues in experimental animals exposed to high

concentrations. There are few data available from actual occupational or environmental exposures to xylenes that warrant their consideration as important environmental health hazards for the general public. The NIOSH xylene standard is 100 ppm as a TWA for up to a 10-hour workday and 40-hour workweek, with a ceiling concentration of 200 ppm (National Institute for Occupational Safety and Health 1975). For additional information on the health effects of volatile hydrocarbons, the reader is referred to the Refinery Operations section of this report.

Nonvolatile Hydrocarbons. The aliphatic nonvolatile hydrocarbons are generally considered to be biologically inactive, but there are indications that paraffins from decane to hexdecane may influence the tumorigenicity of carcinogenic hydrocarbons on epithelial tissues. The C₁₀ through C₁₆ alkanes applied in high concentrations increase the activity of carcinogenic polycyclic aromatic hydrocarbons (PAHs) and may act as weak tumor promoters. On the other hand, alkanes with C₃₀ may inhibit the carcinogenicity of PAHs.

The nonvolatile olefins, following photodecomposition in the atmosphere, produce epoxides and peroxides that are suspected carcinogens, co-carcinogens, tumor-promoters or both. These decomposition products were shown to be tumorigenic in experimental animals following skin painting and subcutaneous injection. The epoxides, which are oxygenated components of nonvolatile olefins, are known to be ciliotoxic and are shown to inhibit the lung clearance mechanism in experimental animals. The exact chemical composition of these nonvolatile olefins is not known and further research is needed. Extensive studies have been carried out on the carcinogenic activity of many epoxides (mono-, di-, and poly-), β -lactones, hydroperoxides, and peroxides in a variety of test systems. These systems include skin application in mice, subcutaneous injection in mice and rats, and intragastric intubation in rats (Van Duuren 1969). Further research is needed to better understand the mode of action of these hydrocarbons. Additional information on these substances may be found in the section of this report concerning refinery operations.

Particulate Hydrocarbons. These constitute approximately 20 to 65 percent of the organic particulate matter present in polluted urban air (Hoffman and Wynder 1977). Polycyclic aromatic hydrocarbon particles are among the most extensively studied compounds found in polluted air. The great interest lies in the fact that several are known animal carcinogens and some are suspected carcinogens for man. PAHs are the primary mutagenic compounds in crude petroleum and their concentration increases as the boiling range of the petroleum fuels increases. The major potentially carcinogenic PAHs identified with certainty in air pollutants are aromatic hydrocarbons with four, five, and six benzene rings. The relative carcinogenicity of PAHs

are listed in Table 42 (Hoffman and Wynder 1977). Also identified in urban air are traces of 11H-benzo(b)fluorene, 5H-benzo(a)fluorene, 7H-benzo(c)fluorene, and benzo(ghi)fluoranthene, which are considered noncarcinogenic. Urban air also contains traces of several alkylated PAHs. (The PAHs emitted from heavy duty diesel- and gasoline-powered engines are discussed above.)

PAHs have been shown to be carcinogenic in various in vivo tests. These tests have included bioassays on mouse skin, subcutaneous mouse tissue, mouse cervix, and newborn mice. Fractionation studies on urban pollutants suggest that PAHs may play an important role in the overall carcinogenicity and tumor-initiating activity of urban pollutants in experimental animals. These effects are under investigation in experimental animals, following exposure via subcutaneous administration, oral administration, inhalation, or bladder implantation.

Benzo(a)pyrene (BaP), a known carcinogen, is the most widely studied PAH. Estimated emissions for BaP in the U.S. are listed below (Hoffman and Wynder 1977):

Source	Nationwide Estimated BaP Emissions (tons/year)
Vehicles	40-50
Gasoline-powered	20-25
Diesel fuel-powered	20-25
Heat and power generation	450-500
Coal	400-500
Oil	2-3
Gas	44
Wood	40
Total estimated emissions	1,000-1,200

The contribution of BaP from transportation sources is 4 percent of the total, but is entirely a result of oil and gas activities and use, while the contribution from oil and gas combustion for heat and power amounts to approximately 4 to 5 percent of total estimated

TABLE 42

POLYNUCLEAR AROMATIC HYDROCARBONS FROM VARIOUS SOURCES

Name	Structure	Carcinogenicity	Ambient ^a Air	Diesel- Engine Heavy- Duty ^b	Gasoline ^c Vehicles American	Diesel ^d Vehicle
Benz(a)anthracene		very weak carcinogen	+	+	+	+
Chrysene		very weak carcinogen	+	+	+	+
Pyrene		no carcinogen	+	+	+	+
Fluoranthene		no carcinogen	+	+	+	+
Benzo(a)pyrene		strong carcinogen	+	+	+	+
Benzo(e)pyrene		very weak carcinogen	+	+	+	+
Perylene		no carcinogen	+		+	
Benzo(e)acephenanthrylene		weak carcinogen	+			
Benzo(j)fluoranthene		moderately strong carcinogen	+			
Benzo(k)fluoranthene		no carcinogen	+			
Benzo(ghi)perylene		no carcinogen	+	+	+	+

TABLE 42 (Concluded)

Name	Structure	Carcinogenicity	Ambient ^a Air	Diesel- ^b Engine Heavy- Duty	Gasoline ^c Vehicles American	Diesel ^d Vehicle
Dibenzo(cd,jk)pyrene		no carcinogen	+			
Indeno(1,2,3-cd)pyrene		very weak carcinogen	+		+	
Caronene		no carcinogen	+		+	+
Dibenzo(g,h)pyrene		moderately strong carcinogen	+			
Dibenzo(e,l)pyrene		moderately strong carcinogen	+			
Dibenzo(a,i)pyrene		moderately strong carcinogen	+			
Dibenzo(a,e)pyrene		very weak carcinogen	+			
Dibenz(a,g,h)acridine		weak carcinogen	+			
Dibenz(g,j)acridine		very weak carcinogen	+			
Benzo(c)phenanthrene		moderately strong carcinogen		+		+
Benzo(b)fluoranthene		weak carcinogen		+		

Note: + Indicates relevance to medium/source.

^aSource: Hoffman and Wynder 1977.

^bSource: Spindt 1977

^cSource: U.S. Environmental Protection Agency 1978c.

emissions. This reflects the existence of a potentially greater health hazard for individuals exposed to BaP from oil and gas consumption in the transportation sector, compared to using oil and gas for heat and power in the industrial, commercial, and utility sectors. BaP emissions from gasoline-powered automobiles have been significantly reduced in the U.S. through the use of newer model cars and implementation of emissions control regulations. The data presented below supports this expected reduction in BaP levels (Hoffman and Wynder 1977):

Source	BaP (ug/gallon fuel consumed)
Uncontrolled car (1956-1964)	170
Uncontrolled car (1966)	45-70
Emission controlled vehicles (1968)	20-30
Advanced systems	10

It is estimated that as much as 30 percent of the BaP in exhaust gases can be attributed to BaP in gasoline fuels (Bergman and Colucci 1968). Benzo(a)pyrene production in gasoline-powered automobiles at an air-to-fuel ratio of 20 to 1 is 30 times higher than that at a ratio of 14 to 1. As vehicles accumulate mileage in normal consumer use, there is an increase in deposits formed in the combustion chamber, which influences total hydrocarbon exhaust emissions. This may reflect a negative differential health hazard for the poor (undocumented), who generally own older and less well-maintained automobiles, especially in the densely populated low-income sections of urban communities.

The quantity of benzo(a)pyrene emitted from stationary combustion sources is highly dependent on the efficiency of combustion, and not on the fuel. In specific areas, the relative contribution of any given source may differ significantly from that implied by the nationwide figures (e.g., the vehicular source may be the major contributor in suburban areas where large stationary sources are absent).

With particulate hydrocarbons, namely PAHs, their effect on human health depends on the particle size. The major source of carcinogenic particulate organic matter in polluted air is controlled combustion that produces particles 0.1 to 10 μm in diameter. "Lung-damaging" components are considered to be particles 0.25 to 10 μm in diameter. Particles less than 0.25 μm are retained to a low degree in the lung, and particles with diameters greater than 10 μm lodge in the upper respiratory tract and do not reach the bronchi.

Because practically all combustion leads to the formation of unknown traces of carcinogenic PAHs and the particles generated are primarily 0.1 to 10 μm in diameter, it has been assumed that particulate organic matter will be partially deposited in the bronchial tree, especially at the bifurcation (National Academy of Sciences 1972). This thesis has been substantiated by experimentally demonstrating that BaP and other PAHs are readily eluted from soot samples recovered from the human lung (Falk et al. 1958).

Polycyclic aromatic hydrocarbons of weak or mild carcinogenicity that are present in the polluted air have been suggested to act as co-carcinogenic or anticarcinogenic agents. Whenever two or more agents present in the air are applied simultaneously or sequentially under experimental conditions, they may interact in a variety of ways so as to alter each other's effects. This modifying nature of carcinogenic and anticarcinogenic agents should be clarified.

The polycyclic aromatic hydrocarbons and heterocyclics, e.g., olefins, constitute a group of known carcinogens, co-carcinogens, or anticarcinogens that are present in the particulate phase of polluted air. However, the extent of their contribution to the incidence or promotion of human lung cancer in particular is unknown. Other agents--such as tumor-promoting, co-carcinogenic, and noncarcinogenic, but tumor-initiating agents, and carcinogens other than aromatics (e.g., asbestos, benzene)--probably contribute to the PAH-caused total human health hazard. These agents and their physical and chemical characteristics, modes of action, oxidation products and intermediates, and target organs are poorly understood. Extensive research is being undertaken to investigate the unknowns mentioned above.

In vivo and in vitro carcinogenesis/mutagenesis studies for whole gasoline, diesel fuel, and heating oils are attempting to identify synergistic, additive, and cumulative effects of other gaseous pollutants in the presence of known carcinogens. An example of such research includes a study initiated to study comparative mutagenic activity of organics from combustion sources (Claxton and Huisingsh 1979). The results are presented in Table 43. This study demonstrates how bacterial mutation systems can be used to provide relative potency comparisons as well as qualitative comparisons for the

TABLE 43

SPECIFIC ACTIVITY AND RELATIVE POTENCY
OF VARIOUS COMBUSTION ORGANICS

Strain	Specific Activity ^a (Relative Potency) ^b				
	Cigarette Smoke	Roofing Tar ^c	Diesel Vehicle	Gasoline Vehicle	Residential Heater
TA98	Negative 98.2 (0.3)	Negative 98.7 (0.3)	1,225.2 (8.9) 1,367.1 (4.0)	137.8 (1.0) 341.9 (1.0)	90.5 (0.7) 152.5 (0.4)
TA1538	Negative 90.6 (0.6)	Negative 34.4 (0.3)	347.2 (7.2) 468.0 (3.2)	48.4 (1.0) 144.1 (1.0)	40.2 (0.8) 71.4 (0.5)
TA1538	Negative Negative	Negative 36.5 (0.5)	178.5 (6.0) 206.2 (2.6)	29.8 (1.0) 79.1 (1.0)	18.4 (0.6) 33.0 (0.4)
TA1535	Negative Negative	Negative Negative	Negative Negative	Negative Negative	Negative Negative
TA100	Negative ? ^d	Negative 420.0 (1.8)	1,270.1 (6.5) 881.7 (3.9)	196.6 (1.0) 228.0 (1.0)	200.0 (1.0) 289.2 (1.3)

^aRevertants per plate at 100 ug of organic material calculated from a linear regression analysis.

^bGasoline vehicle given relative activity of 1.0.

^cFrom retest of organics at lower doses.

^dQuestionable result, to be retested when material is available.

Source: Claxton and Huisinck 1979.

evaluation of complex mixtures. In a recent study conducted for the American Petroleum Institute, it was demonstrated that no. 2 home heating oil does not exhibit positive mutagenic response in Salmonella typhimurium. However, in vitro mouse lymphoma array indicated a significant dose-response, with an increase in mutation frequency both in the presence and absence of metabolic activation. The study results concluded that no. 2 home heating oil has the potential to produce mutations in genetic material (Hazelton Laboratories 1979). It should be noted that the relationship of mutagenic potency and carcinogenic potency is not clear at this time and is a controversial issue in toxicology.

Occupational Exposures. Workers in oil- and gas-fired power plants, automobile garages, and service stations, as well as those in jobs involving diesel and jet fuels, mechanics, and workers handling heavy duty engines may be exposed to PAHs in the workplace. Under normal working conditions, exposure to PAHs can be controlled with the use of protective clothing, masks, respirators, and hand creams or gloves. Accidental occupational exposure is a matter of particular concern. Occupational exposures and related hazards suggest exposure through the skin and inhalation.

Epidemiological evidence suggests that dermal exposure to PAHs causes various skin associated ailments. These include nonallergic dermatitis, cell-mediated hypersensitivity (allergic contact dermatitis), phototoxic and photo-allergic reactions, folliculitis, acne, and pigment changes. Nonallergic dermatitis in workers has been caused by materials containing PAHs such as lubricating and cutting oils. The inflammatory response of the skin to irritants and antigenic agents in man is known as an eczematous reaction. The histological features of acute contact dermatitis are intracellular and intercellular epidermal edema, and in chronic contact dermatitis, the epidermis also is thickened. Clinical response is characterized by erythema and edema that persist longer than a primary irritant response. Continuous exposure of mechanics and service station employees to cutting and lubricating oils may cause acne, characterized primarily by lesions involving the pilosebaceous apparatus of the skin.

The relationship between occupational PAHs exposure via inhalation and pulmonary disease such as chronic bronchitis and emphysema has been studied in great detail. Evidence suggests that airborne polycyclic organic compounds are carcinogenic. Studies of occupational PAH exposures and possible respiratory effects among chimney sweeps, petrochemical workers, and coal workers are known, but data are not available which suggest incidences of lung cancer in workers associated with oil and gas combustion and transportation activities.

Long-term exposure to gasoline and jet fuel has been suggested to cause chronic mental and neurological symptoms. A cross-sectional epidemiological study on jet fuel workers showed intoxication by jet fuel (80 percent aliphatic, 20 percent aromatic hydrocarbon) followed by acute symptoms related to the central nervous system: dizziness, drowsiness, nausea, vomiting, pain during inhalation, feeling of suffocation, slight cough, palpitations and thoracic oppression (Knave et al. 1979). It is not clear what component of the fuel may cause the observed neurasthenic syndrome (i.e., fatigue and emotional instability).

Ambient Exposure. Nonoccupational neoplastic pulmonary effects were summarized by scientists associated with the Committee on Biological Effects of Atmospheric Pollutants--Particulate Polycyclic Organic Matter (National Academy of Sciences 1972). Based on reviews of various epidemiological studies of lung cancer, the committee concluded that:

- o Lung cancer has emerged as the single greatest cause of cancer death in males and a significant cause of death in females in the United States, and its incidence has increased in the last 30 years.
- o A major etiological factor appears to be cigarette smoking; however, smoking does not completely account for the increased incidence of the disease.
- o Urban dwellers have approximately twice as high an incidence of lung cancer as those living in rural areas. Within urban communities, the incidence is greater where more general industrial pollution is present.
- o Polycyclic organic matter, found in cigarette smoke in high concentrations, causes cancer of the lung and other organs in experimental animals, is present in the air in large quantities in industries whose workers have high lung cancer rates, and is present in the air of urban communities.
- o Generally, immigrants have an incidence of lung cancer between that noted for their countries of origin and that of the countries to which they migrate. The higher their ages when they migrate, the closer their rates are to those of their cohorts who remain in the countries of origin. In some of the studies in which the home country had a much higher cancer rate, the rates in persons who left it decreased significantly, even though their cigarette smoking increased. These studies suggest a significant environmental effect operating early in life for lung cancer development.

- o A variety of types of epidemiological studies lead to an estimate of the effect of pollution on the lung cancer death rate of a 5 percent increase per unit increase in urban pollution [as indexed by benzo(a)pyrene with one benzo(a)pyrene unit = 1 ug of benzo(a)pyrene per 1,000 m³ of air].

In short, these results suggest the feasibility and warrant the desirability of further epidemiological studies on airborne carcinogenesis resulting from hydrocarbons emitted during the use of oil and gas. One way to assess the impact of particulate hydrocarbon pollution on lung cancer is to see what happens when pollution is reduced. To see whether particulate hydrocarbon pollution contributes to the development of respiratory cancer, trends in cancer deaths from 1950 to 1970 in London, where particulate pollution declined greatly, can be compared with trends in the rest of England and Wales where the decline was not as pronounced (Higgins 1974).

Hydrocarbon Mixtures

Gasoline. Hydrocarbon mixtures produced and consumed in the U.S. include natural gas, gasoline, kerosene, jet and turbo fuels, and lubricating oils. Gasoline represents the major source of homogeneous hydrocarbons emitted in a mixture of C₄ to C₁₂ hydrocarbons where blend composition* includes paraffins (56.8 percent by weight), olefins (7.9 percent by weight), naphthenes (2.47 percent by weight) and aromatics (benzene 0.12, toluene 21.8, and alkyl benzene 7.0 percent by weight) over a boiling range of 79° to 399°F (26° to 204°C). Acute exposure to gasoline vapors will cause symptoms of intoxication similar to heptane exposure. These include uncontrolled hilarity, stupor, loss of appetite, slight nausea, and a taste resembling gasoline. The concentrations of gasoline hydrocarbons that cause mucous membrane irritations will vary with the concentration and degree of branching of the paraffins, and alkyl derivatives of benzene and olefins. The human response to unleaded gasoline vapor inhalation at temperatures below 230°F (110°C) is described below (Machle 1941):

*API standard.

Concentration (ppm)	Exposure Time	Response
500	1 hour	No effect
900	1 hour	Slight dizziness and irritation of eyes, nose, and throat
2,000	1 hour	Dizziness, mucous membrane irritation, and anesthesia
10,000	20 minutes	Nose and throat irritation in 2 minutes, dizziness in 4 minutes, sign of intoxication in 4 to 10 minutes

Based on the above data, a threshold limit value for gasoline of 500 ppm was recommended (Gerarde 1963a, b).

Human inhalation toxicity data for gasoline vapor exposure are very limited. Inhalation of extremely high concentrations of gasoline vapor can cause narcosis, coma, and sudden death. Death upon acute exposure to gasoline fumes generally is attributed to severe central nervous system depression terminating in respiratory paralysis. Sudden deaths observed in cases of accidental gasoline exposure are attributed to the sensitization of the myocardium to the extent that small quantities of epinephrine may precipitate ventricular fibrillation (Chenoweth 1946). Inhalation of milder concentrations of gasoline vapor usually are characterized by nonspecific anesthetic or narcotic effects with symptoms of headache, vertigo, blurred vision, ataxia, tinnitus, nausea, anorexia, and muscular weakness. Table 44 summarizes the effects of gasoline vapors on humans. Chronic gasoline toxicity data and epidemiological studies for occupational exposures to gasoline vapors are limited.

In general, the symptoms of chronic exposure to gasoline vapor are ill-defined. They may consist of fatigue, muscular weakness, nausea, vomiting, abdominal pain, and weight loss. Exposure also is known to have neurological effects which include confusion, ataxia, tremor, paresthesias, neuritis, and paralysis of peripheral and cranial nerves (Swinyard 1977).

TABLE 44

HUMAN EXPOSURE TO GASOLINE VAPORS

Concentration (ppm)	Exposure Time	Physiological/ Sensory Effect
5,000-16,000	5 mins	Lethal
10,000	10 mins	Nose and throat irritation in 2 mins; dizziness in 4 mins; signs of intoxication in 4-10 mins, definite in- toxication
3,000	15 mins	Dizziness, nausea
2,600	1 hr	Dizziness
2,000	1 hr	Dizziness, mucous membranes irritated and anesthesia
1,000	15 mins	Drowsiness, dullness, numbness
1,000	1 hr	Dizziness, headache, nausea
1,000	30 mins	Eye irritation only
900	1 hr	Slight dizziness, irritation of eyes, nose and throat
550	1 hr	Eye irritation
500	1 hr	Eye irritation
300-700	18 mins	No symptoms
160-270	8 hrs	Eye irritation

Source: Chenoweth 1946.

Cases of repeated, self-induced gasoline intoxication, generally involving higher concentrations of gasoline vapor, could possibly be considered chronic inhalation exposures. Persons engaged in the regular habit of "gasoline sniffing" experience loss of appetite and weight, muscular weakness, and cramps. Other effects reported to result from this practice include abnormal electroencephalograph readings and possible liver and renal damage.

The greatest hazard associated with chronic gasoline inhalation is exposure to the aromatic hydrocarbons, especially benzene. As previously noted, chronic benzene intoxication can result in irreversible systemic effects such as encephalopathy, aplastic anemia, and leukemia. The literature lacks information relating chronic gasoline sniffing to fetal pathological conditions such as liver, kidney, or bone marrow lesions.

The threshold limit value (TLV) for a gasoline is dependent upon the benzene concentration in the gasoline mixtures and the additive or synergistic effect of benzene with other hydrocarbons in gasoline.

Gasoline TLVs were calculated using the American Conference of Industrial Hygienists (ACGIH) method at the former benzene TLV criterion of 10 ppm, as well as the new criterion of 1 ppm (Runion 1977). Results indicated that gasoline containing 1 percent benzene, for example, had a TLV of 30 ppm, whereas the same gasoline with the proposed benzene standard of 1 ppm would have a TLV of less than 150 ppm.

No serious attempt has been made to measure the health risk to the general public as a result of gasoline vapor exposure. Studies have been conducted utilizing large numbers of filling station attendants, tank-truck drivers, garage mechanics, and gasoline loaders, and they have provided no conclusive evidence of harmful health effects due to low level exposures to gasoline vapors. In these studies, a phenol excretion level is used as an index of benzene absorption. This phenol index is particularly susceptible to individual variations in metabolic rates, nutritional status, smoking habits, and dietary intake. The importance of these confounding factors needs to be explored.

Diesel Exhaust. As seen earlier, emissions of volatile hydrocarbons are lower from diesel than from gasoline engines, but use of an oxidation catalyst can substantially reduce most of these emissions from gasoline engines. However, recent analytical studies have shown that particulate emissions in diesel exhaust can be up to 82 times as much as in gasoline exhaust (Springer and Baines 1977). There are several important reasons why increased exposure to particulate matter derived from diesel engines may constitute a potential health hazard (Schreck 1978).

- o Carbonaceous particles from diesel exhaust are reportedly composed in part of high-molecular-weight polycyclic aromatic hydrocarbons.
- o These particles have large surface areas, theoretically enabling them to adsorb large quantities of gaseous exhaust products, most importantly the carcinogenic POMs such as benzo(a)pyrene.
- o The particles themselves may be degraded by atmospheric oxidation to yield lower-molecular-weight POMs which are potentially carcinogenic.
- o Diesel particulates are primarily in a size range (0.2 to 0.3 um mean diameter) which would allow for deposition in the deep lung compartments, and possible retention in the lung.

Diesel exhaust particulates are known to contain the carcinogenic and mutagenic chemical benzo(a)pyrene, among many other potentially hazardous and less well characterized components. The quantities of particulates that may be emitted from both gasoline and diesel cars in 1990 are estimated below (Huisingh et al. 1978):

Percent Diesel New Car Sales 1985-1991	Particulate Emissions in Tons from Gasoline Cars by 1990	Particulate Emissions in Tons from Light Diesel Cars by 1990
0	32,000	0
10	28,000	57,000
25	26,000	155,000

The amount of particulate matter that would be emitted from gasoline cars in 1990, if no diesel cars are sold, is estimated at 32,000 tons. In contrast, as much as 155,000 tons could be emitted by diesel cars if they make up 25 percent of car sales. This estimate assumes no emissions controls on diesel passenger cars. The possible impact of rising diesel usage on atmospheric pollution indicates that an increase in diesel use is likely to increase PAHs in ambient air, resulting in a new source and, conceivably, in an additional health hazard.

In the past few years, diesel exhaust emissions have been extensively characterized. The tests include mutagenicity testing in Salmonella typhimurium, generally taken as strong presumptive evidence for the existence of mutagenic as well as carcinogenic activity. The Ames test has been used to show the relationship between collection and extraction techniques for diesel exhaust emissions, and mutagenic activity of diesel exhausts. Some mutagenic activity was demonstrated in the insoluble basic and acidic fractions of dichloromethane (DCM) extracted particulate samples. However, neutral fractions showed most of the mutagenic activity (U.S. Environmental Protection Agency 1978c).

Direct acting components as well as components requiring metabolic activation were apparent in different fractions, although most of the mutagens were of the direct-acting frameshift type. Studies of direct-acting mutagens are significant because they exclude polycyclic hydrocarbons, which require metabolic activation for expression of mutagenic effects. It was suggested that substituted polynuclear aromatics, namely phenols, ethers, and ketones, were the major components of a neutral fraction.

Investigators in this area have suggested exercising caution before implicating neutral fraction components in diesel exhaust as a major health hazard to man. The results of bacterial mutagenicity assays on diesel and gasoline exhaust have indicated that direct-acting mutagens are formed during combustion. These mutagens are presumed to be substituted polycyclic aromatic hydrocarbons. The mutagenicity of the diesel exhaust was found to be 10 times higher than that of the gasoline exhaust, although the addition of microsome activation enzymes decreased this activity (Lofroth 1979). Mutagenic activity was enhanced in anaerobic assays, presumably due to the presence of nitro compounds (U.S. Environmental Protection Agency 1978c).

Various in vivo studies undertaken to assess potential hazards of diesel exhaust emissions have concluded that:

- o Exposure of rats to diesel particles for 9 months did not result in a toxic effect, although some changes, including a significant increase in lung weight, were observed (Misiorowski 1979).
- o Inhalation of diesel emissions may lead to emphysema in rats and mice (Bhatnager 1979).
- o In comparison to the gasoline engine operating with or without a catalytic converter, the diesel engine produces far greater quantities of carbonaceous particulate material.

These particles are of respirable size and have large surface areas, which allows them to absorb gaseous exhaust products. Among these products are small amounts of irritant gases and, perhaps most significantly, a large portion of potentially carcinogenic polycyclic organic matter, e.g., benzo(a)pyrene. Benzo(a)pyrene has been shown to account for 20 percent of the carcinogenic activity of diesel exhaust condensate observed in skin painting tests with mice (Grimmer 1979).

Schefner (1979) demonstrated that lung cancer appears to be more prevalent and far advanced in diesel-exposed hamsters than in controls. This poses the potential risk of delivery of adsorbed gases into the lung by carrier particles. In turn this may lead to extensive localization of harmful materials in the lung, with the accompanying threat of emphysema and cancer. In addition, fibrotic changes may occur, leading to reduced lung compliance and/or obstruction.

Investigators have for many years attempted to show that exposure to automotive emissions may lead to the development of cancer. Indeed, it was shown several decades ago that both diesel and gasoline engine exhausts contain carcinogenic polycyclic aromatic hydrocarbons such as benzo(a)pyrene. Since that time, chronic studies have been initiated which involve the inhalation of total diesel emissions by rats and hamsters. Under the conditions employed, these experiments have failed to produce tumors of the respiratory tract. On the other hand, there is evidence of serious damage to respiratory tissues. Rats exposed to diesel exhaust for 20 months displayed extensive particulate accumulations in the lungs, accompanied by vesicular emphysema, and beginning interstitial fibrosis. Hamsters developed similar problems, in addition to the presence of cuboidal metaplasia. It is not known whether such tissue damage is reversible or if it may shorten lives. In addition, a high incidence of skin cancer has been shown to occur in mice following dermal application of the particulate exhaust fraction from diesel and gasoline engines.

A series of in vivo studies with several animal species inhaling diesel exhaust indicated the existence of clearance mechanisms for diesel particulates. Among guinea pigs inhaling diesel exhaust, several exposure-related changes were seen including increased pulmonary flow resistance, increased lung-weight-to-body-weight ratios, sinus bradycardia, and damage to the alveolar walls. The reversibility of these lesions or the degree of functional impairment which accompanies them has not been determined. A series of in vivo mutagenesis studies in progress may provide definitive data on this problem.

Biochemical and metabolic effects associated with exposure to diesel exhaust emissions are not known. Studies involving DNA bonding, effects on collagen production, and inhibition of BaP metabolism, along with research on uptake, distribution, metabolism and excretion, will provide valuable information to assess diesel exhaust emissions and human health hazards. Work is also underway to measure and identify behavioral and neurophysiological effects in experimental animals.

An objective of the epidemiological investigation of diesel exhaust emissions is to demonstrate that an increased use of diesel vehicles is environmentally acceptable. With recent occupational mortality and morbidity studies on groups, including railroad workers, truck drivers, miners, heavy duty equipment workers, diesel mechanics, and trash collectors, it has not been possible to isolate diesel emissions as a singular component contributing to the excess deaths and adverse (carcinogenic) health effects occasionally observed. The London Transport study completed in 1957 (Raffle 1957) found no increased cancer incidence among bus garage drivers. This study has been criticized for poor documentation of exposure levels and for poor control regarding the workers' smoking habits. Large population-based studies are just emerging, since large populations that have been exposed to ambient levels of light duty diesel emissions have not previously existed in the U.S. This also is true of well-controlled investigations of worker populations, since quantitative exposure data have not been available. Most studies are conducted with coal miners who are exposed to underground diesel exhaust emissions. One such study concluded that, for coal miners exposed to diesel emissions: there were no relationships between respirable particles and shift changes in pulmonary functions; there were no relationships between NO_2 and shift change in pulmonary function; and smokers suffered greater pulmonary function decrements over a workshift than ex-smokers or nonsmokers. Coal miners exposed to diesel emissions in addition to the ordinary mine atmosphere show some decrements in their lung function over a work shift (Reger et al. undated). Another study on coal miners exposed to diesel emissions reported symptoms of persistent cough, phlegm, and exacerbation of cough and phlegm. Aside from dyspnea and wheezing, long-term diesel exhaust exposure was associated with a tendency toward deteriorating health for coal miners (Reger and Hancock undated).

There is no way to place in perspective the comparative hazards of diesel and overall automobile emissions. Diesel exhaust is a noxious mixture with the potential to produce serious lung disease, behavioral alterations, biochemical changes, and decrements in pulmonary function. Its risk as a human carcinogen, however, is unquantified. When looked upon in light of what we know regarding the potential health effects of noncatalyst-treated gasoline exhaust, the

impact of diesel fueled emissions remains unclear. Presently, firm data suggesting an increased carcinogenic threat from the substitution of diesel- for gasoline-powered light duty vehicles are not available. Further epidemiological research must be pursued and studies with laboratory animals must be conducted to characterize cause-and-effect relationships and exposure-response parameters.

Carbon Monoxide

Air emissions of carbon monoxide (CO), resulting from the use of oil and gas in transportation and combustion, accounted for approximately 65, 77, 80, and 78 percent of total emissions in 1968, 1970, 1972, and 1974, respectively. This large air pollution burden has been studied in detail and the effects of carbon monoxide pollution are well summarized elsewhere (U.S. Department of Health, Education, and Welfare 1970).

Carbon monoxide is an odorless, colorless gas that offers no warning before actual poisoning occurs. Thus, severe accidental CO poisoning is fairly common. With increasing concentrations, the usual sequence of signs and symptoms are headache, dizziness, weariness, flickering eyes, ringing in the ears, nausea, vomiting, difficult breathing, muscular weakness, collapse, unconsciousness, and death. No overt signs are to be expected from exposure to carbon monoxide at even the highest concentrations found in the ambient air (50 to 100 ppm). However, concern has been expressed regarding the possibility that exposure to ambient concentrations may decrease physical or mental acuity or interfere with the function of an organ already suffering oxygen deficiency, such as a diseased heart. With humans, CO has been shown to negatively affect vigilance, reaction time, estimation of time, coordination and tracking, sensory processes, and complex intellectual behavior.

CO principally interferes with oxygen transport by combining with hemoglobin. Carboxyhemoglobin, thus formed, gradually accumulates, and with time, eventually reaches a plateau or equilibrium unless death occurs. Thus, the level of carboxyhemoglobin in the body is a function of both the concentration of the inhaled gas and duration of exposure. The general population is not continuously exposed to high CO levels, and carboxyhemoglobin diminishes to background when exposed persons leave the area of contamination such as traffic, or when ambient levels subside at night. There is general agreement that, for normal individuals, exposure to low levels is entirely reversible and causes no lasting dysfunction. The relationship between exposure to CO pollution and the resulting carboxyhemoglobin is not immediately obvious because of the time delay between exposure and the buildup of carboxyhemoglobin levels in the blood and its effects on tissues.

A number of studies have investigated the relationship between cigarette smoking and carbon monoxide exposure. Inhaling clearly increased the smoker's intake of carbon monoxide. In addition, the effects of CO on cardiovascular disease have been studied extensively in experimental animals and to some extent in human subjects. These studies indicate that carbon monoxide can affect the heart: decreasing the probability of survival of persons who have a myocardial infarction and possibly other cardiovascular diseases; aggravating an existing circulatory condition, particularly angina pectoris and peripheral arteriosclerosis; and causing unfavorable changes in the healthy person. In addition, evidence suggests it may be a factor in the onset and progression of cardiovascular disease.

Occupational Exposure. Carbon monoxide exposure is possible for automobile mechanics, traffic controllers, and tunnel construction workers. Signs and symptoms of acute CO poisoning are headaches, dizziness, drowsiness, nausea, vomiting, collapse, coma, and death. Loss of consciousness occurs at about the 50 percent carboxyhemoglobin level. Recovery from acute poisoning usually occurs without sequelae unless tissue hypoxia was severe enough to result in brain cell degeneration. Severe CO poisoning has been reported to permanently damage the extrapyramidal system, including the basal ganglia.

The present Federal standard is 50 ppm (55 mg per m³). A standard recommended by the National Institute for Occupational Safety and Health is 35 ppm with a ceiling value of 200 ppm. The 35 ppm would limit carboxyhemoglobin formation to 5 percent in a nonsmoker engaged in sedentary activity at a normal altitude. The protective measures that workers can undertake include using gas masks where CO levels are not exceedingly high and using self-contained air ventilation systems in areas with high concentrations.

Photochemical Oxidants

The photochemical process that forms secondary pollutants through the interaction of primary pollutants and sunlight results in a number of irritating or toxic chemicals. Ozone and peroxyacyl nitrates are toxic when inhaled or absorbed through surface contact. If present in sufficient concentrations in the air, these gases can cause death. At sublethal concentrations, they cause physiological malfunctions or anatomical lesions.

Investigation of the acute toxicity of ozone began as early as 1904. At first, work was mainly concerned with mortality, gross examination of the lung for evidence of inflammation, wet weight-dry weight ratios for evidence of edema, and histopathological examination (Coffin and Stokinger 1977). Brief exposure to ozone at higher-than-ambient concentrations has been known to cause edema and acute

inflammatory responses. The long-term either continuous or intermittent exposure to ozone appears roughly proportional to the time and dose of the ozone exposure in the experimental animals. Long-term, exposure-related anatomical changes consist of an increase in the number of pulmonary alveolar macrophages; deposition of fibrous elements; changes in the lung elasticity; thickening of the terminal airway and respiratory bronchiolar walls; accumulation of lymphocytes, plasma cells, and fibroblasts in the peribronchiolar tissue; metabolic alterations in the endothelial cells of the interalveolar capillaries; pathological changes such as necrosis, replacement of the respiratory epithelium, reversion of connective tissue to a less cellular appearance in the terminal bronchioles; fibroplastic proliferation; and a flattening and smoothing of the bronchiolar epithelium.

Despite extensive investigation, there is still no generally accepted explanation of the mechanism or mechanisms through which ozone exerts its toxic action. Experimental exposure of human volunteers to ozone has produced symptoms of cough, substernal soreness, pharyngeal irritation, dyspnea, headache, and general discomfort. However, these symptoms do not persist after the exposure.

The systemic effects ascribed to ozone exposure include the following: changes in elements in the circulating blood, decrease in brain serotonin, increase of the RNA-to-DNA ratio in the liver, transitory increase in liver weight and alkaline phosphatase, morphologic alterations of the parathyroid gland, and increased sleeping time from sodium phenobarbitol. Extensive research on possible mutagenic effects has been inconclusive.

Occupational exposure to high levels of ozone in industries using oil and gas is unlikely. Exposure of the general population and related health effects are discussed above.

Sulfur Oxides

Air emissions of sulfur oxides from transportation and oil-and gas-fired boilers are negligible. Hence, the health effects of sulfur oxides emissions are not detailed in this section. Briefly, sulfur oxides health effects include aggravation of the respiratory diseases of asthma, chronic bronchitis, and emphysema; reduced lung function; and irritation of eyes and the respiratory tract. These are discussed in the Transportation and Storage section of this report.

Lead

The major sources of lead exposure are air, food, and water, with an estimated average intake of 0.12 to 0.35 mg per day. The

important absorption routes for man and animals are ingestion and inhalation. In adults, from 5 to 10 percent of ingested lead and 20 to 50 percent of inhaled lead may be metabolically absorbed into the body (Goldsmith and Friberg 1977). Studies of occupational lead poisoning show that symptoms include loss of appetite, a metallic taste in the mouth, constipation and obstipation, aneuria, pallor, malaise, weakness, insomnia, headache, nervous irritability, muscle and joint pains, fine tremors, encephalopathy, and colic (Mayers 1969). With lead colic, there may be severe abdominal pain and gastrointestinal cramps. Three types of toxicity are documented: gastrointestinal cramps, central and peripheral nervous system effects, and anemia. Kidney disease, excessive frequency of hypertension, and vascular disease have also been reported.

Lead can interfere with the synthesis of heme, thereby altering the urinary or blood concentration of enzymes and intermediates in heme synthesis or their derivatives. Thus, lead poisoning can lead to an accumulation of nonheme iron and protoporphyrin-a in red blood cells; an increase in l-aminolevulinic acid in blood and urine; an increase in urinary coproporphyrin, uroporphyrin, and porphobilinogen; inhibition of blood aminolevulinic acid dehydratase; and an increased proportion of immature red blood cells. Table 45 summarizes the effects of lead poisoning in humans following exposure to lead either by inhalation or ingestion.

Various studies have found substantially higher levels of lead in blood samples from urban dwellers than from rural residents. It has been suggested that reducing the amount of lead inhaled would significantly reduce the body's burden of lead.

Children are more vulnerable to lead exposure than are adults. Their ingestion is distributed to a smaller tissue mass and their gastrointestinal absorption is estimated to be 25 percent, compared to 8 percent for adults (Karhausen 1973). Some children also are exposed to lead when they eat dirt and paint chips. In addition, their more rapid growth rate and metabolism make them more vulnerable to lead poisoning. Urban children have higher blood lead levels than rural children. When children suffer acute lead poisoning, much of the increase in the body's burden of lead and most of the damaging effects to the nervous system are due to lead paint, air pollution (partly as a result of the combustion of leaded gasoline), and the high lead levels of dirt in streets, parks, and other areas where children play. The biological limits proposed to protect children and adults are shown in Table 46 (Zielhuis 1973).

Occupational Exposure. Policemen, firemen, taxi drivers, vehicle tunnel attendants, garage mechanics, and service station attendants are examples of occupational groups who work out-of-doors, but

TABLE 45
EFFECTS OF LEAD POISONING

Disease; Affected Organ or System	Physiological Changes	Symptoms
Anemia	Reduced red blood cell life span, reticulocytosis, occurrence of basophilic stippled cells in peripheral blood	Irritability, fatigue, pallor and sallow complexion
Gastrointestinal sequelae (intestinal colic)	No major physiological effects	Nausea often without vomiting, constipation, and headache before or about the time of onset of colic
Peripheral and central nervous system	Peripheral neuropathy; extensor muscles of the hand and feet are often involved	Loss of motor function but little loss of sensory function; extensor weakness precedes wrist drop or palsy
Encephalopathy	Cardiorespiratory arrest following ingestion of lead by children	Acute effects--seizures, coma and death. Chronic effects--loss of motor skills and of speech, development of behavioral disorders
Encephalopathy	Absorption of alkyl lead	Psychosis
Neuropathy	Progressive and irreversible loss of kidney function, with progressive azotemia and occasional hyperuricemia with or without gout	Children have developed renal dwarfism, hypertension, marked retention of urea, and low urinary concentration. Faconi syndrome observed in some children. Nephritis in adults

TABLE 46

PROPOSED LIMITS FOR LEAD
AND ITS BIOCHEMICAL INDICES^a

	Individual Upper Limit	Group Average	Unit
<u>For Adults</u>			
Blood lead (PbB)	40	25	µg Pb/100 ml
Urine ALA ^b	6	3	mg/liter urine
Blood ALA dehydratase	20	30	Percentage decrease from 100% at: 10 µg PbB/100 ml
<u>For Children</u>			
Blood lead (PbB)	35	20	µg Pb/100 ml
Urine ALA	5	3	mg/liter urine
Blood ALA dehydratase	30	40	Percentage decrease from 100% at: 1 µg Pb/100 ml

^aThese limits were proposed as guidelines for public health hazard appraisal. They should not be regarded as fine lines discriminating innocuous from harmful environments; however, if the limits are exceeded, the possibility of undue acute effects or chronic sequelae increases. The data for population groups should be interpreted by experts who can judge the representativeness of the population sample. Single values moderately exceeding upper limits in individuals should cause awareness and caution; the measurement should be repeated.

^bALA - amino levulinic acid.

Source: Zielhuis 1973.

are nonetheless exposed to lead from the combustion and use of oil and gas products. The primary source of this exposure is the lead salt emitted from internal combustion engines that burn leaded gasoline. A Public Health Service (1965) survey showed that these workers are placed in atmospheres containing varying amounts of lead for their 8-hour workday. Some samples indicated levels that even approach the Federal standard for lead and its inorganic compounds, which is 0.2 mg per m³ as a time weighted average. It is evident, from the results of many blood samples collected from workers and the public, that there is a high rate of lead absorption on the job.

The Federal criteria document recommends that occupational exposures be limited to a time weighted average value of 0.15 mg per m³. This is the level of airborne lead that will result in biochemical indices showing acceptable lead absorption. It also recommends, based on the acceptable urinary lead level of 0.15 mg per liter, a threshold value of 0.10 mg per m³ (National Institute for Occupational Safety and Health 1972).

Blood lead level is the single sound criterion for interpreting the acceptability of lead absorption. Other indices that are useful in the assessment of worker health include aminolevulinic acid (ALA) and coproporphyrin assays, as well as examination of blood for hemoglobin, reticulocytes, and stippled cells. Blood lead and urine lead are good indices of the momentary absorption of lead, but are not necessarily indications of a body's lead burden. Bone lead is probably more indicative of total body burden, but it is not feasible to sample bone for a routine lead assay.

Exposure of the general population and workers to lead has been controlled to some extent through the use of unleaded gasoline in motor vehicles as discussed earlier. Exposure of children to the lead in ingested paint scalings and chips can be successfully mitigated by reducing the lead content of paint. For oil processors, handlers, and those in the end use work force, exposure to lead and lead alkyls can be reduced with full body work clothing and caps and the use of dust and fume masks or air respirators.

Nickel

Nickel is a trace metal found in crankcase oils and as a persistent metal in waste oils generated at automotive centers. Workers are exposed to nickel through handling lubricating oils in garages, service stations, and waste oil recovery stations. In these cases exposure is through skin contact, and to a lesser extent, inhalation. The Federal standard for nickel metal and its soluble compounds is 1 ug per m³. Nickel is probably carcinogenic, producing an increased incidence of cancer of the lung and nasal passages. Effects on the

heart muscle, brain, liver, and kidney have been seen in animal studies (National Academy of Sciences 1975).

Additives

Tetraalkyl Lead. Tetraalkyl lead compounds are used as anti-knock agents in gasoline and ethylene dibromide is usually added to gasoline along with these lead additives. Tetraethyl and tetramethyl are the most commercially important tetraalkyl lead compounds. The occupational groups susceptible to exposure to these compounds include gas station attendants, storage tank cleaners, gasoline additive workers, garage mechanics, and airplane machinists. Public exposure to lead alkyls is negligible.

Tetraalkyl lead may enter the human system in three ways: inhalation, ingestion, and skin contact. Ingestion is of minor significance when workers are aware of the hazard and use ordinary precautions. Inhalation of the vapor and percutaneous absorption of the liquid of such compounds cause the following systemic effects (U.S. Department of Health, Education, and Welfare June 1977). The absorption of a sufficient quantity of tetraethyl lead, whether briefly at a high rate, or for prolonged periods at a lower rate, may cause acute intoxication of the central nervous system. Mild degrees of intoxication cause headache, anxiety, insomnia, nervous excitation, and minor gastrointestinal symptoms with a metallic taste in the mouth. The most noticeable clinical sign of tetraethyl lead poisoning is encephalopathy, which may give rise to a variety of symptoms including mild anxiety, toxic delirium with hallucinations, delusions, convulsions, and acute toxic psychosis. Physical signs are not prominent, but bradycardia, hypotension, increased reflexes, tremor, and slight weight losses have been reported. No peripheral neuropathy has been observed. When the interval between the termination of (either brief or prolonged) exposure and the onset of symptoms is delayed (up to 8 days) the prognosis is guardedly hopeful, but when the time interval is short (a few hours), an early fatal outcome may result. Recovered patients show no residual damage to the nervous system, although recovery may be prolonged.

No cases of poisoning from absorption of tetramethyl lead have been reported. The compound responsible for almost all cases of organic lead poisoning is tetraethyl lead. Animal experimentation, however, indicates that a similar intoxication can be caused by tetramethyl lead. The Federal standard for tetraethyl lead is 0.075 mg per m³ and for tetramethyl lead is 0.07 mg per m³.

Ethylene Dibromide. As mentioned earlier, ethylene dibromide (EDB) is added to gasoline along with lead additives to assist in the removal of lead from the engine after combustion. Of the 33×10^6

pounds of EDB produced each year, approximately 80 percent is used with lead gasoline additives (Air/Water Pollution Report 1977). As a component of lead additives, however, it seems likely that EDB will be phased out of gasoline as the lead concentration is reduced. EDB now comprises about 25 percent of the total lead additive mixture. Quantitatively, it would appear that EDB vaporization is negligible from such diluted solutions.

EDB has been shown to be toxic, carcinogenic, mutagenic, and teratogenic, as well as a sterility inducer in numerous animal studies. The National Institute for Occupational Safety and Health has recommended that workplace EDB exposure be limited to a ceiling level of 1 mg per m³ of air, a reduction from the current limit of 20 ppm (145 mg per m³). Human data on the carcinogenic and sterilizing effects of EDB alone are lacking. However, even the low airborne levels of EDB that may vaporize from gasoline may be associated with some increased risk of adverse health effects.

Indoor Air Pollution

The health hazard from an indoor pollutant is a function of the following parameters:

- o The levels at which it occurs indoors,
- o The frequency with which it occurs indoors,
- o The extent to which individuals are exposed to the pollutant, and
- o The exposure-effect relationship of the pollutant.

These parameters are potentially quantifiable by monitoring and sampling indoor air pollutant levels. Instruments needed to characterize and measure indoor levels are not available. The instruments that are commercially available to measure and monitor ambient levels of air pollutants and workplace pollutants cannot be used successfully because of various limitations.

Research priorities have only recently focused on indoor air pollution. The results of these studies may indicate that air pollution levels are higher inside than outside. Indoor pollutants of concern include:

- o Carbon monoxide, nitrogen oxides, and sulfur oxides;
- o Tobacco smoke and its products;

- o Chlorinated hydrocarbons and organophosphates in pesticides;
- o Fluorocarbons in propellants;
- o Lead, cadmium, arsenic, and aluminium; and
- o Radionuclides.

This listing is in order of importance, based on the pollutant's ubiquity in nonworkplace indoor environments, the extent to which substantial health hazards have already been identified, and the extent to which the existence of the hazard and a lack of data suggest that further research is needed.

Indoor air pollution issues related to oil and natural gas end uses are primarily associated with the presence of the gaseous pollutants NO, NO₂, CO, evaporative hydrocarbons, and radioactivity, and to a lesser extent, SO₂.

Nitrogen Oxides

Nitrogen oxides in indoor air may present a human health hazard in light of reported indoor concentrations. The NO₂ level in a gas kitchen is significantly higher than in an electric one. Two studies, one in England and the other in the U.S., reported that gas kitchens had NO₂ concentrations six to seven times higher (Melia et al. 1978).

This difference between gas and electric kitchens may explain the association between respiratory disease and gas cooking reported for school children in England. The boys and girls from homes in which gas was used for cooking were found to have more coughs, "colds going to the chest," and bronchitis. This "cooking effect" was assumed to be independent of the effects of age, social class, population density, levels of SO₂ outdoors, and types of fuel used for heating (Melia et al. 1977).

NO₂ principally associated with gas appliance operations has been found within the following range (Melia et al. 1977):

<u>Duration</u>	<u>NO₂ Levels (peak)</u>
1-hr average	450-950 ug/m ³
1-hr	1,900-2,800 ug/m ³

These values can be compared with short-term exposure effects studied in the range of 228 to 815 ug per m³--levels known to contribute to an excess risk of acute respiratory disease in the absence of

excessive long-term exposure (Melia et al. 1977). The range of 1-hour average NO₂ concentrations given above for gas-fired appliances is within this range of a potential risk of acute respiratory disease. (However, the American Gas Association does not support this relationship.)

A review of published and unpublished data related to Chattanooga, Tennessee, concludes that (French 1975):

- o Exposure to prolonged levels of nitrogen dioxide, ranging from 113 to 395 ug per m³, in combination with short-term exposures of 301 to 1,203 ug per m³, may contribute to an excess risk of acute respiratory disease and the residual effects from this exposure may last for as long as 4 years.
- o Repeated short-term exposures at 228 to 815 ug per m³ may contribute to an excess risk of acute respiratory disease in the absence of excessive long-term exposures.
- o Prior high short-term and long-term exposures to NO₂, coupled with continuous excessive short-term exposures, might trigger the onset of chronic respiratory disease symptoms.

Other studies have compared the incidence of reported respiratory illness in households cooking with gas and electricity, but they fail to conclusively support the above relationship. Further field studies to determine the effects of short-term NO₂ exposure in houses using gas-fired appliances are needed.

The unvented gas space heater has been shown to contribute NO₂ to the indoor air. A study conducted in Florida homes found that gas space heaters contribute 222 ppb NO₂, which is above the U.S. Primary Air Quality standard (Palmer and Tomezyk 1979). The Consumer Product Safety Commission proposed banning the heaters in February 1978 because of their ability to produce CO and to deplete room oxygen. The proposed ban was not related to a possible NO₂ hazard.

Another aspect of indoor NO₂ pollution is the need to monitor and evaluate nitric acid, nitrates, and nitrosamine concentrations. There is also a need for studies of blood level concentrations of methemoglobin in residents of homes with and without gas-fired appliances.

Carbon Monoxide

Indoor CO levels range from 1,000 to 4,000 mg per hr (400 to 1,000 mg per Kcal), depending upon stove operation. The carbon monoxide gas is relatively unreactive and decays slowly. It is also

emitted from gas-fired furnaces during normal operations, from leaky furnaces, and from attached garages.

The special hazards of indoor CO buildup are widely known. Studies have shown that indoor concentrations of carbon monoxide often reach potentially hazardous levels, and smoking is an important contributor. Internal combustion engines used in ice skating rinks and school buses are sources of indoor CO known to have caused symptoms of drowsiness, headaches, and nausea in school children. Carbon monoxide levels greater than 50 ppm have been measured in houses with faulty indoor combustion sources (Cote et al. 1974).

An ad hoc committee, established in 1972 by the Bureau of Community Environmental Management, reviewed the effects of CO on human health with the specific objective of developing recommendations for residential standards. Committee members concluded that continuous exposure should not exceed 15 ppm (resulting in about 2.6 percent at equilibrium in the blood of nonsmokers). This level was considered to allow both for the higher CO concentration tolerance of smokers and the increased susceptibility of cardiac patients.

Considering the ambient standard to be nine ppm for 8 hours, indoor concentrations should not be allowed to raise the baseline air content by more than six ppm. For comparison, 15 ppm has been proposed as the short-term public limit by the National Academy of Sciences (1970). These results are of particular concern when extrapolated to a large population using stoves and heating systems and space heaters fueled with oil and natural gas.

Sulfur Oxides

Gaseous emissions of sulfur dioxide from gas ovens under various burner and ventilation conditions have been shown to be in the range of 15 to 110 μg per m^3 (Hollowell et al. 1976). No available data suggest respiratory hazards due to exposure to indoor sulfur oxide concentrations. Additional work is necessary to show any cause-effect relationship at indoor levels. Information documented for outdoor levels of SO_x suggest the synergistic effects of SO_2 with particulates and of SO_2 with sulfates in producing both acute and long-term respiratory system problems; however, the adverse impacts of SO_2 alone at common ambient levels are poorly understood.

Even though SO_2 concentrations have been shown to be lower indoors than outdoors, the mechanism of SO_2 depletion may be a cause of concern since the process involves the oxidation of SO_2 to sulfates with potential hydration to form acid mists. The sulfate particles which tend toward micron- and submicron-sized aerosols may be important indoor air pollutants. These suspended sulfate

particles may remain indoors for some period of time, presenting a persistent health hazard. Further research is needed to study the chemical composition, concentration, and human uptake and impact of indoor sulfates.

Hydrocarbons

Evaporative and particulate hydrocarbon emission levels associated with oil- and gas-operated household appliances are not well known. Saturated aliphatic hydrocarbons present indoors include: the gaseous methane, propane, and butane; and liquid hydrocarbons from pentanes C_5 through C_{16} . Methane, the principal component of natural gas, is biologically inert, while other aliphatics are known asphyxiants or irritants. In general, compounds in the series from propane through octanes show increasingly strong narcotic properties, although the thresholds are high. Based on the composition of natural gas burned during cooking and the length of exposure to combustion products in homes, the following equivalent exposure times are given:

Constituents of Natural Gas	Formula	Time that Occupants Could Breathe the Products of Combustion for a 2-Hour Roast
Methane	CH_4	1 Hr, 45 minutes.
Ethane	C_2H_6	10 Minutes, 5 seconds
Propane	C_3H_8	2 Minutes, 53 seconds
Isobutane	C_4H_{10}	36 seconds
Butane	C_4H_{10}	50 seconds
Isopentane		43 seconds
Pentane	C_5H_{12}	Less than 1 minute
Heptane	C_7H_{16}	Less than 1 minute

Intermittent, chronic exposure to the products of combustion or partial combustion of these evaporative hydrocarbons could lead to cumulative health effects. The nature and extent of this problem

should be studied further. The roles of natural gas contaminants such as benzene and metals also are unknown. They could pose potential hazards at long-term, low-level exposures, resulting from the operation of gas appliances. These hydrocarbons, in the presence of indoor nitrogen oxide, may produce secondary pollutants of unknown types and quantities. Aldehydes also may arise from cooking operations and their indoor levels or effects are unknown. All of these problems should be researched.

Radioactivity

The effects of exposure to low levels of ionizing radiation have been studied for many years. Recently, the state of knowledge in this area was summarized in a report of the Committee on the Biological Effects of Ionizing Radiations of the National Academy of Sciences (1980).

The levels of radon released from natural gas combustion in the average home have not been thoroughly quantified. Presumably they vary from near zero to high levels resulting in over 30 mrem per year (in terms of the dose-equivalent to the bronchial epithelium for persons exposed to radon as a result of natural gas combustion for cooking and space heating). Radon levels in gas presumably vary with the degree of radioactivity strata from which the gas was withdrawn. Since natural gas is transported long distances, this could be a pervasive and serious problem.

The section of this report on indoor pollution lists known emission levels for radon associated with oil and gas use. As indoor exposures to radon are known to occur at high levels from a number of other sources, indoor radon emissions (including those from the use of oil and gas) constitute a national problem that threatens to grow worse. This problem requires immediate steps to assess its full ramifications and to develop control options (Inside Washington Publishers 1980).

Confounding Factors

In addition to the effects of pollutants, one must consider the interaction of indoor pollutants with variables such as indoor temperature and humidity. Studies by the Community Health and Environmental Surveillance System (CHESS) of the U.S. Environmental Protection Agency (1978f) and other studies that have been cited imply that ambient air pollutants cause more aggravation of respiratory disease at high temperatures. One study concluded that increasing the relative humidity of occupied spaces from 20 to 50 percent reduces the relative incidence of respiratory conditions among school children (Green 1975). Thus, the use of humidifiers mitigates the effects of indoor pollutants.

Scientists are concerned about human exposure to myriad organic chemical substances released in the home, such as vapors, liquid phase, dust from aerosol sprays, household cleaners, and insecticides. Based on clinical observations, it has been suggested that home pollutants affect immune response systems, promote collagen, aggravate cardiovascular diseases, and even cause mental illness. More data are needed to conclusively show any relationship among indoor air pollutants generated from oil and gas appliances in the home and other health hazards.

To effectively assess the role and impact of indoor air pollutants, one must await actual exposure measurements performed with proper instruments, and a demonstration of the extent to which exposures overcome physiological defense mechanisms to produce adverse effects.

Summary of Research Needs

Several research needs were identified in the discussion above on health effects. There, these were placed in context with supportive documenting justification.

The following summary draws some of this information together, highlighting the research needs.

Stationary Source Combustion

- o Assessment of health effects from air emissions of sulfur, nitrogen, hydrocarbons, and particulates emitted by oil- and gas-fired power plants, as compared to coal-fired power plants (see text for specific information needs).
- o Development of an epidemiological information base and monitoring methods for workers exposed to indoor emissions from oil-fired boilers and gas-fired heaters and dryers.
- o Development of biological tests for routine medical surveillance of specific hydrocarbon compounds and complex mixtures.
- o Development of in vivo tests to study the occupational health effects of inhalation, ingestion, and dermal exposures to distillate and residual heating oils.
- o Study of the development of neurobehavioral and reproductive effects following exposure to distillate and residual oil mixtures and fractions in laboratory animals.

- o Study of the long-term health effects of chronic exposure to ambient levels of specific pollutants that accompany the use of oil and gas.
- o Design of clinical studies to test low-level exposures to SO₂ and NO_x in volunteer populations.

Mobile Source Combustion

- o Study of the toxic effects of exhaust pollutants generated from automobiles fitted with pollution control devices by in vivo and in vitro tests (with emphasis on specific, untreated pollutants).
- o Implementation of occupationally-based epidemiological studies to provide morbidity and mortality data regarding gasoline and diesel exhaust exposure. The sampling should be large enough to detect the low probabilities involved. These should be compounded with the Howard Medical School study of 30,000 railroad workers.
- o Initiation of community-based epidemiological studies to provide information on any morbidity and mortality effects of diesel exhaust exposure. These should be compared with the results of occupational studies.
- o Design of in vivo and in vitro methods to quantify and compare exposures to diesel and gasoline exhaust (with emphasis on cancer and emphysema).
- o Development of biological tests to monitor workers exposed to higher concentrations of gasoline, diesel fuels, and lubricating oils, individually or in groups.
- o Development of guidelines for proper fuel use and cleanliness at self service gasoline stations.
- o Initiation of diesel exhaust inhalation exposure studies in animals using various dose levels to detect neurotoxicity, reproductive effects, cardiovascular function impairment, and threshold dose levels for toxic response.
- o Evaluation of diesel exhaust mutagenicity by in vivo and in vitro tests that use standard methods precisely and are reproducible.
- o Evaluation of carcinogenesis using various fractions of diesel exhausts in in vitro systems.

- o Evaluation of the carcinogenic, co-carcinogenic, and tumor promoting and inhibiting potential of diesel exhaust emissions in laboratory animals following different exposure routes.
- o Assessment of the toxic effects of diesel exhausts in light of variation in fuel and engine operating parameters.
- o Development of animal test models to ascertain the fate, clearance, and transport mechanism of inhaled and/or ingested diesel particulate matter.
- o Implementation of parallel toxicity studies with diesel and gasoline exhausts to compare relative hazards and public health implications.
- o Study of the effects of chronic intoxication in occupationally exposed populations, investigating behavioral, reproductive and cardiovascular hazards.
- o Study of the carcinogenic potential of ethylene dibromide, a gasoline additive, at various concentrations.
- o Study of olefins, naphthenes, and certain other organic constituents of gasoline to determine their potential toxicity.
- o Determination of the effects of benzene with other hydrocarbons and additives in gasoline by in vivo and in vitro studies.
- o Quantitative assessment of the health risks due to gasoline vapor exposure.
- o Development of tests to study chronic gasoline intoxication in laboratory animals.
- o Study of the carcinogenic and dermatosis hazards of lubricating oils via skin contact by skin painting experiments.
- o Determination of the neurobehavioral, reproductive, and other systemic effects following inhalation of and dermal exposure to diesel fuels in laboratory animals.
- o Study of the synergistic effects of CO and smoking as well as the cumulative effects of carbon monoxide exposure in the workplace.
- o Collection of exposure data for defined occupationally exposed populations in automobile and related industries.

- o Study of the biological fate of diesel and gasoline fuels in laboratory animals and the effects of these on biotransformation and detoxification.

Indoor Air Pollution

- o Study of the effects on human behavior and health caused by indoor sulfates, oxidants, nitrosamines, dioxins, and nitrates emitted from oil and gas sources or formed from subsequent chemical reactions.
- o Determination of effects from short-term NO₂ exposures associated with effects in home occupants using oil- and gas-fired appliances.
- o Study of synergistic and/or cumulative health effects of chronic, low-level exposures to indoor pollutants generated from oil- and gas-fired appliances.
- o Evaluation of effects of indoor oil and gas emissions on children, the elderly, the diseased, and persons with pre-existing physiological or mental disorders.
- o Development of models for calculating human exposure to indoor air pollutants, taking into consideration outdoor and workplace exposures to similar pollutants and individual health histories.
- o Design of epidemiological studies and data collection systems to study the morbidity in occupants exposed to oil- and gas-generated indoor pollutants.
- o Development of human exposure standards for indoor pollutants based on exposure levels for both indoor and outdoor sources of oil and gas emissions.
- o Design of studies to evaluate effects of air pollution on the public, considering the totality of atmospheric, occupational, and indoor exposures to pollutants emanating from oil and gas use.
- o Characterization of household exposure to indoor air pollutants in light of frequency (i.e., continuous, intermittent, infrequent, persistent, etc.) and subsequent effects following different routes of exposures.
- o Study of the absorption and inhalation potentials and subsequent fate and deposition of oil and gas end-use-generated indoor air pollutants in man by in vivo tracer studies.

- o Documentation of the nature and extent of radon radiation from indoor oil and gas use. Sources for study include gas range surface burners and ovens, oil and gas space heaters and furnaces, air conditioning units, dryers, and water heaters.
- o Determination of the actual dose-equivalent exposures received from all of the above oil and gas related sources in relation to other indoor sources.

ECOLOGICAL EFFECTS OF OIL AND GAS USE

Ecological effects associated with oil and gas use are less severe than, or perhaps less noticeable when compared with, impacts of other fossil fuel uses (e.g., coal and other facets of the oil and gas industry). Oil and gas end uses primarily impact the ecosystem, particularly vegetation. The effects of end use combustion on aquatic ecosystems are minimal and the aquatic system is covered extensively in other parts of this report, so this subject is not discussed here. However, this section includes a brief discussion of the effects of waste oils on land and water biota.

Effects on Vegetation

The effects of air pollutants on vegetation generally are discussed in terms of effects on individual plants. These effects are diagnosed to be either highly visible or subtle. Visible effects are identifiable morphologically, while subtle effects can be observed only when growth or physiological changes occur in a plant. Descriptions of injury to vegetation by air pollutants are widely documented in various review articles. Only the significant points in the symptomology are summarized below.

At high concentrations, nitrogen oxides (particularly nitrogen dioxide) affect vegetation by acutely injuring plants. Low concentrations are known to increase chlorophyll levels, but long-term, low-level exposures may cause early leaf senescence and abscission. Ozone exposure causes a variety of leaf markings, forming stipple, fleck, and necrotic areas on broad leaves, grasses, and conifer needles. Plants sensitive to ozone include oat, petunias, pinto beans, potatoes, radishes, soybeans, sycamores, tobacco, tomatoes, white ash, and white pine. Plants resistant to ozone damage are beets, geraniums, gladiolus, maples, mint, peppers, and rice. Exposure to sulfur dioxide results in visible damage to sensitive plants such as alfalfa, apple, barley, cotton, giant ragweed, pine, squash, and wheat. Plants resistant to sulfur dioxide exposure include cantaloupe, celery, corn, oak, and rhododendron. Peroxyacetyl nitrate sensitive plants are annual bluegrass, petunia, pinto bean, and romaine lettuce, while resistant plants are broccoli, chrysanthemum, corn, cotton, and sorghum.

The most discussed source of lead enrichment in soils and plants is tetraethyl lead, an antiknock additive in gasoline. The lead content of unwashed plant material from both sides of traffic lanes near major highways is 5 to 10 times that of plants from adjacent fields (Kloke 1975). With stagnant wind conditions, the lead content in roadside plants has increased by as much as 100 times. This contamination has been shown to be external. The lead content of

plants decreases asymptotically with increasing distance from the traffic lanes and, as a rule, reaches a normal level 100 meters from the highway. The magnitude of the lead content is primarily determined by traffic density, exposure time, wind direction, and specific plant factors. The enrichment of lead on plants is accompanied by lead enrichment in soil and animals such as field mice.

The cadmium content can be increased by diesel vehicles and the use of heating oil in industries, rising from 0.2 to 2 mg per kg. In plants, the increase may be from 0.5 to 1 mg per kg. The cadmium content of 0.22 ppm in the soil at a distance of 32 meters from traffic lanes is increased to 1.45 ppm at a distance of 8 meters (Lagerwerff and Specht 1970). This increase is attributed to the age of the street, traffic density, and wind conditions.

Hydrocarbons historically have been recognized as phytotoxic air pollutants. Ethylene pollution, to a large extent, is attributed to emissions from internal combustion engines. Ethylene has affected vegetation adversely at atmospheric concentrations of 1 ppm or less. A concentration as low as 0.05 ppm has caused malformation in certain plants--and this concentration is well within the range measured in ambient air. While other unsaturated hydrocarbons such as acetylene, propylene, and butylene produce effects similar to ethylene's, the effects occur at concentrations 60 to 500 times that of ethylene. Naturally produced ethylene serves as a hormone that regulates plant growth and development and other processes such as fruit ripening. Thus, ethylene is unique, serving either as an endogenous plant regulator or a serious phytotoxic air pollutant, depending on its concentration.

In general, rural areas have ethylene levels lower than 5 ppb; however, higher levels observed in urban areas are consistent with traffic density and are highly dependent upon topography and meteorological conditions. Peak ethylene concentrations in urban areas have ranged from <5 ppb to as high as 700 ppb, while mean concentrations are considered to be much smaller. With the advent of the catalytic converter, in use on U.S.-built cars since 1975, it is expected that ethylene levels will begin to decrease since the internal combustion engine is responsible for more than 90 percent of the ethylene in ambient air. Ethylene standards have been proposed by various associations, but due to a lack of sufficient data, no standard has been universally adopted. The 1-hour maximum standard recommended by the American Industrial Hygiene Association ranged from 0.25 to 1 ppm (287.7 to 1,150 $\mu\text{g per m}^3$) and the 8-hour maximum ranges from 0.05 to 0.2 ppm (57.5 to 230 $\mu\text{g per m}^3$).

Polycyclic organic matter apparently does not induce cancer-like tumors in plant tissues following external exposures. Various investigators have reported absorption of PAHs, such as benzo(a)pyrene,

phenanthrene, anthracene, pyrene, anthanthrene, benzo(e)pyrene, chrysene, perylene, benzo(a)anthracene, benzo(ghi)perylene, dibenz-(a,h)anthracene and coronene, from soil into lettuce, kale, spinach, leeks, and tomatoes (National Academy of Sciences 1972). These hydrocarbons are known to be present in the ambient air and automotive exhaust. (See previous parts of the End Use section for the pervasiveness of these substances with respect to oil and gas end use emissions.) Benzo(a)pyrene also has been detected in various cereal grains. How much of this contamination is due to oil and gas end use activities or other industrial sources remains undetermined. Also unknown are the long-term exposure effects of massive doses of polycyclic compounds on plant growth, development, and reproduction.

Effects on Biota

Effects on plants and animals are usually not limited to one specific area, but are observed over a great distance because of the nature of oil and gas end use activities (e.g., transportation and combustion). For the oil and gas industry as a whole, these effects are most severe with oil and gas exploration, extraction, refining, and transport and storage activities. Thus, discussion of the effects of hydrocarbon emissions and effluents is contained in the sections of this report dealing with such industrial activities. The potential terrestrial and aquatic hazards due specifically to waste oil disposal are discussed below.

Impacts of Waste Oil Disposal

Waste oils and their proper disposal represent a major area of concern. Indiscriminate disposal of waste oil is potentially detrimental to terrestrial and aquatic ecosystems. Prior to 1972, virtually no information existed on the effects of waste oil on land and in the aquatic environment. Waste oil is introduced in the environment primarily through four routes: road oil use (spreading), land disposal, dumping in sewers, and burning.

Recent modification in refinery technology has provided the capability to recycle these oils. Collection, storage, and transportation of these wastes will continue to be constraints until there is some economic incentive favoring recycling.

Land disposal of used oil is a time-honored practice that affects surface water and land when the discharge is without adequate treatment or proper disposal. The soil is known to be an excellent medium for growing microorganisms, thus it is capable of assimilating and decomposing organic matter. Soil microbes, with proper application rates and conditions, can assimilate complex organic mixtures

from waste oils. It is suggested that high molecular weight, viscosity and crystallinity are properties that inhibit biological decomposition. Medium-molecular-weight hydrocarbons such as kerosene and light motor oils oxidize easily, but aromatic hydrocarbons are more resistant.

Adding large amounts of waste oil to land creates anaerobic conditions and the efficiency of decomposition is minimized. Large oil applications are often toxic to plants. The volatile fractions of these oils have great penetrating power, entering plants and seeds and producing a narcotic effect. This effect is the result of a mechanical obstruction that prevents the plants from obtaining sufficient moisture and air. Land disposal of waste oils has been viewed as a blessing for some types of soils because the long-term effect upon soil is to improve its physical and chemical properties by increasing organic matter and nitrogen content, decreasing its volume-to-weight ratio, and increasing moisture holding capacity (Dotson et al. 1974; U.S. Environmental Protection Agency 1974).

The effects of waste oils in the freshwater medium are studied by determining acute and chronic waste oil toxicity levels for tissue accumulation levels in fish. The studies also characterize virgin oils, waste oils, intermediates, and by-products to identify potential toxic components. The nonvolatile components of waste oils include about 76 percent saturated hydrocarbons, 4 percent aromatic hydrocarbons (comprised primarily of alkyl benzenes and polynuclear compounds), 3 percent volatile hydrocarbons, 4 percent polar compounds, and 15 percent particulate material. Metals present include lead (18,500 ug per gm), and zinc (1,350 ug per gm) (Hedtke 1974).

The volatile components of waste oil are alkyl benzenes and naphthalenes, but the freshwater soluble fractions of waste oil are different, containing 80 percent polar compounds, 3 percent saturated compounds, and 14 percent aromatic compounds. The metal concentrations are as high as 16,000 ug per liter of zinc; 4,400 ug per liter of lead; and 200 ug per liter of molybdenum, selenium, arsenic, chromium, nickel, iron, manganese, copper, and cadmium. Waste oil is essentially free of chlorinated compounds.

Short-term mortality tests indicate that the approximate level lethal to freshwater fish is 0.1 to 1.1 percent by volume of total oil and a chronic "no effect" level is between 0.08 and 0.35 percent by volume of a water soluble fraction stock solution. Tissue residue analyses indicate a significant accumulation of normal hydrocarbons, zinc, lead, and cadmium; with no accumulation of aromatic hydrocarbons above the ug per gm level.

Used crankcase oil is demonstrated to be toxic to large marine organisms such as the coot, clam, oyster, and lobster. LD50 concentrations in these organisms range from 1 to 5 ppm, while the toxicity to phytoplankton, zooplankton and larval fish ranged from 10 to 50 ppm (Rogerson 1974). Sub-acute studies show that waste crankcase oil causes morphological changes in estuarine fish as well as oysters and scallops.

Studies that characterize sublethal effects and community structure changes are needed before standards can be set to protect marine biota. It has been suggested that fish can produce mutagenic metabolites from PAHs and that used crankcase oils, which are released into the terrestrial and aquatic environment, may represent a considerable mutagenic threat (Payne et al. 1978). Further research is needed on effects in the following areas: reproductive success of marine organisms, freshwater invertebrates, and more sensitive freshwater fishes; survival and community structure in marine and freshwater field conditions; the sensitivity of organisms to other pollutants or to disease; and the synergistic effects of waste oil introduced into domestic treatment facilities.

For additional information on the ecological effects of products of oil and gas combustion, of evaporative hydrocarbons, and of waste effluents and leachates, the reader is referred to the Refinery Operations, Transportation and Storage, and Onshore Development sections of this report.

Summary of Research Needs

- o Study the biological transport and fate of lead, vanadium, and nickel in soil and their bioaccumulation in plants and food chains, especially with respect to man.
- o Determine ways to use waste oils in land farming similar to the way oil is used in refinery sludges. (Technology transfer is needed in this area.)
- o Determine the pervasiveness of the automobile owner's clandestine practices for disposing of waste oil and identify mitigating control strategies.
- o Identify the extent to which leachates emanate from road surfaces coated with waste oil and their effects on aquatic systems.
- o Identify the extent to which evaporative hydrocarbons emanating from road surfaces contaminate nearby crops and other vegetation.

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TRANSPORT AND TRANSFORMATION EFFECTS

The air polluting effects of oil and gas use are discussed in this section, since emissions from transportation and oil and gas combustion contribute significantly to total air pollution. The effects of end use activities on water are insignificant when compared with other oil and gas technology sequences such as transportation and storage, refinery operations, and onshore and offshore development. Thus, the sections of this report relating to those technologies discuss water pollution.

The atmospheric emissions from oil and gas end use activities are subjected to a variety of physical and chemical influences that may lead to the formation of objectionable products, or the objectionable products may be converted into harmless compounds. The pollutants released from stationary sources and mobile source combustion include primary pollutants (e.g., nitrogen oxides, carbon monoxides, hydrocarbons, sulfur oxides) and secondary products (e.g., photochemical oxidants). Research on air transport and transformation effects is helpful in determining the nature of precursors, the mechanisms of reactions, and the effects of emissions on air quality.

Among the emissions, evaporation of gasoline alone accounts for a mixture of hundreds of species of organic molecules. Even more complicated are the secondary transformation products found in automobile exhausts and emissions from oil- and gas-fired boilers used to generate electricity, process heat, and steam. These products are further exposed to changes through oxidation, ozonation, and photochemical reactions that result in formation of smog, haze, ozone, and peroxyacetyl nitrates. The photochemical air pollution outlined below delineates, in broad terms, the directions that should be taken in collecting data on and researching transformation mechanisms.

Photochemical Air Pollution

When exposed to sunlight, hydrocarbons react with other compounds in the atmosphere, producing ozone and other photochemical oxidants. The chemistry of oxidants formation is described in detail in several publications (National Academy of Sciences 1976b, 1977).

The description presented below is a highly simplified version of the complex chemical reactions leading to photochemical air pollution. It serves to underscore the pivotal role that hydrocarbons and other emissions of end use technologies may have in these processes.

The major photochemical oxidants--ozone (O_3), nitrogen dioxide (NO_2), and peroxyacetyl nitrate (PAN)--are secondary pollutants formed in the atmosphere under favorable conditions. Ozone, present

in the highest concentrations, is the product of a reaction in which common diatomic oxygen (O_2) reacts with molecular oxygen (O) in the presence of a third molecule or action (M):

M is usually a nitrogen compound or oxygen. The atomic oxygen (O) reactant is generated largely from the photolysis of nitrogen dioxide (NO_2):

The reaction mechanism is completed by the reaction of the two reaction products to regenerate nitrogen dioxide and diatomic oxygen:

The above reactions are the mechanism for atmospheric ozone formation, but alone they do not account for ozone accumulation.

Photochemical hydrocarbon reactions affect the relative rates and the concentrations of products of the above reactions. Modeling and smog-chamber simulations show significant oxidant formation when reactive hydrocarbons are present. Hydrocarbons photochemically regenerate free radicals that react with oxygen to form alkylperoxy and hydroperoxy free radicals. These radicals react with NO to form NO_2 :

Hydrocarbons are oxidized in the process. These hydrocarbon reactions essentially "pump" the primary reaction of NO_2 photolysis by scavenging the reaction's NO product and making available more NO_2 reactant. In the process, atomic oxygen is made available for ozone and other oxidant formation. The amount of pumping, and thus the amount of oxidants formed, depends on the concentration and reactivity of the hydrocarbons present.

Table 47 presents a comparison of reactivities of different types of hydrocarbons. Hydrocarbons are classified with respect to oxidant-related reactivities in urban atmospheres in Table 48. Note that alkenes (olefins), benzene derivatives, and aldehydes have the highest reactivities. Methane, ethane, propane, and benzene do not participate in these reactions. These reactivity data reflect rates

TABLE 47

COMPARISON OF REACTIVITIES OF DIFFERENT TYPES OF ORGANICS

Substances of subclass	Reactivity with respect to designated effects, 0 to 10 scale						Overall reactivity
	Ozone or oxidant	Peroxy-acyl-nitrate	Formaldehyde	Aerosol	Eye irritation	Plant damage	
C ₁ -C ₃ paraffins	0	0	0	0	0	0	0
Acetylene	0	0	0	0	0	0	0
Benzene	0	0	0	0	0	0	0
C ₄ + paraffins ^a	0-4	0 ^b	0 ^b	0	0 ^b	0	1
Toluene (and other monoalkylbenzenes)	4	ND ^c	2	2	4	0-3	3
Ethylene	6	0	6	1-2	5	+ ^b	4
1-alkenes ^d	6-10	4-6	7-10	4-8	4-8	6-8	7
Diolefins	6-8	0-2	8-10	10	10	0 ^b	6
Dialkyl- and trialkylbenzenes	6-10	5-10	2-4	+ ^e	4-8	5-10	6
Internally double-bonded olefins	5-10	8-10	4-6	6-10	4-8	10	8
Aliphatic aldehydes	5-10	+ ^e	+ ^e	ND ^c	+ ^e	+ ^e	--

^aAveraged over straight-chain and branched-chain paraffins.^bVery small yields or effects may occur after long irradiations.^cNo experimental data available.^dIncludes measurements on propylene through 1-hexene, 3-ethyl-1-butene and 2,4,4-trimethyl-1-pentene.^eEffect noted experimentally, but data insufficient to quantify.

Source: U.S. Environmental Protection Agency 1980.

TABLE 48

CLASSIFICATION OF ORGANICS WITH RESPECT TO OXIDANT-RELATED
REACTIVITY IN URBAN ATMOSPHERES

Class I (Low reactivity)	Class II (Moderate reactivity)	Class III (High reactivity)
C_1 - C_3 paraffins ^a Acetylene ^a Benzene Benzaldehyde ^a Acetone Methanol Isopropanol Tert-alkyl alcohols ^a Methyl acetate ^a Methyl benzoate Ethyl amines ^a N, N-dimethyl formamide ^a Perhalogenated hydrocarbons Partially halogenated paraffins Mono, dichlorobenzenes Methyl ethyl ketone	Tert-monoalkyl benzenes Cyclic ketones Tolualdehydes Tert-alkyl acetates ^a 2-Nitropropane ^a C_4 + paraffins, cyclo- paraffins ^a Ethanol Prim, sec C_2 + alkyl N, N-dimethyl acetamide ^a n-alkyl C_5 + ketones ^a	Prim-, sec-, monoalkyl benzenes Dialkyl benzenes Styrene N-Methyl pyrrolidone Partially halogenated olefins Aliphatic olefins Tri-, tetra-alkyl benzene Methyl styrene Branched alkyl ketones Unsaturated ketones ^a Aliphatic aldehydes ^a Diacetone alcohol Ethers ^a 2-Ethoxy-ethanol

^aCurrently classified as not photochemically reactive under Los Angeles County Rule 66 and similar regulations.

Source: U.S. Environmental Protection Agency 1980.

of formation rather than resulting peak oxidant concentrations. With lesser reactive hydrocarbons, the same reactions occur at a slower rate over a longer period of time.

A number of conditions affect the formation and buildup of ozone concentrations. Moist air significantly aids ozone formation. In the absence of hydrocarbons, an equilibrium is established among ozone, nitric oxide, and nitrogen oxide. Concentrations of these compounds and reactive hydrocarbons change diurnally in response to available sunlight. Atmospheric particulate components, such as metal oxides and carbon particles, have a catalytic effect on many photooxidation reactions.

Besides O_3 , several other compounds are known photochemical oxidants, including NO_2 , hydrogen peroxide (H_2O_2), organic peroxides, organic hydroperoxides, and peroxyacetyl nitrate. Organic peroxides have the general formula $ROOH$. The major peroxyacyl nitrates are peroxyacetyl nitrate (PAN) and peroxybenzoyl nitrate (PBN). (Actually, this nomenclature is inappropriate for these structures--better names would be acetyl peroxyxynitrate and benzoyl peroxyxynitrate.)

Atmospheric hydrocarbon measurement data are deficient. Most available data concern only total hydrocarbon concentrations measured by flame-ionization detectors (FID) (U.S. Environmental Protection Agency 1980b). Nonmethane hydrocarbons (NMHC) are measured by gas chromatographic separation of methane from total hydrocarbons, followed by FID measurement of methane and total hydrocarbons in the air sample. NMHC data are obtained by subtracting methane from total hydrocarbon concentrations. Since the FID responds to organically bound carbon in compounds other than hydrocarbons, the measurement of NMHC may more appropriately be termed nonmethane organic compound (NMOC) measurement (U.S. Environmental Protection Agency 1980). FID techniques have been associated with high measurement errors and variability. This must be considered when NMHC data are compared with exposure data from toxicity studies and used for air quality monitoring. It is apparent that FID measurements may be inadequate for the complete characterization of hydrocarbons in ambient air.

Single Source Pollution

Air pollution caused by gaseous effluents from single or small groups of stacks has been extensively studied. It is regarded as a local problem (except that tall stacks contribute to the long distance transport of pollutants). Primary emission concentrations of concern generally occur at distances ranging from the immediate vicinity of the stack to those on the order of several kilometers. Maximum ground-level concentrations tend to occur within this range

but not adjacent to the stack. The transport and transformation effects related to a single emission are well described in the refinery operations section of this report. A large number of stack emissions spread over a large urban area produce a different type of air pollution problem. Variables such as wind speed, humidity, and temperature affect the resulting pollutant concentrations.

Ozone formation is not commonly observed in coal-fired power plant plumes. However, dispersed in urban areas, particles released from the combustion of coal may have a direct influence on oxidant formation. Hydrocarbons adsorb onto these particles. In metropolitan areas such as Houston, atmospheric hydrocarbons are paraffinic (least reactive and have minor effects on public health). Irradiation of hydrocarbons adsorbed on these airborne particles initiates the formation of olefinic hydrocarbons (more reactive than their precursors in terms of photochemical processes). It is possible that there is some synergism between the irradiation and catalytic constituents of the supporting particles (Nahm 1976).

Indoor Pollution

The two major sources of indoor air pollution are infiltration from outdoor ambient air and generation of pollutants in the indoor environment due to activities such as cooking, heating, and smoking. Pollutants entering buildings from outdoor ambient air include SO_2 , NO_x , CO, HC, oxidants, and suspended particulates. Other pollutants of outdoor origin for which researchers have considered indoor and outdoor concentrations have included the respirable fraction of particles, free metals, biological aerosols, CO_2 , carbon disulfide, hydrogen sulfide, and peroxyacetyl nitrate. For almost all outdoor-generated pollutants, researchers have found that indoor concentrations are lower than those outdoors, except in the upper floors of buildings adjacent to heavily-traveled streets.

The concentration, residence time, and decay rates of indoor pollutants depend on building ventilation and the indoor climate. Apparently, no important research has dealt with indoor chemical formation of secondary pollutants (e.g., sulfates and nitrates).

In general, the area of chemical transformation and fate of indoor pollutants has not been addressed in depth. Data on indoor emissions of criteria pollutants and their distribution and behavior are limited to measurements on the production of carbon monoxide and nitrogen oxide in gas stoves. This scarcity is probably a function of the technological difficulties involved in measuring the fugitive, uncontrolled generation of indoor air pollutants from gas stoves, space heaters, and old, leaky furnaces fueled with oil and gas.

Sulfur dioxide emissions have been attributed to faulty, oil-fueled heating plants in buildings and homes. Various investigators have suggested that the SO_2 concentration inside a building is a function of the ambient outdoor concentration. They have found indoor SO_2 levels to be lower than outdoor concentrations. This reduced level is attributed to the SO_2 adsorption by walls, ceilings, and other interior surfaces. The role of higher relative humidity and its affect on SO_2 levels inside a house or commercial building is not known. In addition, the dynamics and the extent of transformation of SO_2 to sulfate within a dwelling is essentially unknown. Normally, outdoor transformation is a result of the relatively long reaction time for $\text{SO}_2:\text{SO}_4$, rather than the short residence time of SO_2 in the indoor environment.

Carbon monoxide levels also are suggested to be lower indoors than outdoors. CO is relatively unreactive and decays much more slowly than SO_2 . Indoor CO emissions are likely to be from gas-fired appliances, leaky furnaces, and attached garages. Indoor smoking also contributes CO, causing the concentration to increase to six or seven times the background level.

The General Electric Company (1972) investigated the CO behavior in two high rise buildings and reported that indoor CO concentrations were lower than those outdoors at heights lower than 100 feet above the roadway; while at higher elevations, CO concentrations were higher indoors than outdoors. This was attributed to the entrapment of CO within the building. It has been demonstrated that carbon monoxide emissions from a gas stove have a significant effect on indoor CO levels (Geomet 1977). Table 49 illustrates the results from one such survey. This table indicates that CO concentrations were differentially dependent upon background or outside concentrations and indoor stove use. Lawrence Berkeley Laboratory measurements lend support to this result. In houses where higher CO concentrations were found, the problem was traced to unvented space heaters or heating stoves, to oil- or gas-fired furnaces used for central heating, and to combinations of these sources.

Nitrogen oxide concentrations found indoors are attributed to both infiltration from the outdoor environment and to emissions from gas-fired household heating and cooling systems. In a field study conducted in Hartford, Connecticut, investigators found that more NO than NO_2 was generally generated from gas stoves (Cote et al. 1974). NO was found to behave much like monitored CO, with peaks associated with rush hour automobile traffic.

Indoor NO and NO_2 concentrations, to the extent that they arise from outdoor-generated pollution, depend upon a building's

TABLE 49

SUMMARY OF INDOOR AND OUTDOOR CO DATA

House Number	Sampling Period	Daily Average CO Concentration in Each Location $\mu\text{g}/\text{m}^3$					Total Stove (oven plus burners) Use (mins/day)	Number of Days of Valid Data
		Kitchen Over Stove	Kitchen 1 m From Stove	Living Room	Bed-room	Outside		
1	Spring - Summer	--	4,490	4,070	4,170	3,480	198	9
	Fall - Winter 1st half	4,190	3,520	3,230	--	1,670	106	4
	Fall - Winter 2nd half	4,790	4,210	--	3,830	2,310	(Unavailable)	6
2	Spring - Summer	3,000	--	3,080	2,900	2,940	43	3
3	Spring - Summer	4,310	--	3,210	2,680	2,230	37	13
	Fall - Winter 1st half	7,820	6,420	5,070	--	3,380	66	6
	Fall - Winter 2nd half	7,130	6,620	--	5,500	2,500	115	8
4	Fall - Winter	9,070	9,000	8,190	--	2,410	201	6

Source: U.S. Environmental Protection Agency 1977d.

proximity to sources generating the pollutants. No research information is available on indoor mechanisms for determining nitrate and nitrosamine formation.

Hydrocarbon emissions from indoor uses of oil and gas have not been documented. Unmeasurable, low levels of volatile and particulate hydrocarbons may be emitted during gas stove cooking and oil- or gas-fired heating. The hydrocarbon transport and transformation effects are not known. Formation of ozone may be possible, provided hydrocarbons and NO_x are present indoors under favorable conditions. This unknown should be studied in detail.

Indoor air quality monitoring technology is not currently available. For monitoring and characterization purposes there is a strong reliance upon the techniques and instruments developed for ambient air and occupational health monitoring. Adaptation and development of new instrumentation methods would be essential for assessing indoor air quality. Many indoor-generated pollutants are emitted in a "fugitive" manner, i.e., they enter the indoor atmosphere through uncontrolled evaporation from surfaces, leaks from faulty combustion systems, from gas stove burners, or pilot lights on stoves.

Indoor air pollutant levels vary with the following activities of occupants: opening and closing of doors and windows; use of heating, ventilating, and air conditioning systems; and use of household sprays, fumigants, cleaners, and polishes.

Indoor air quality is also affected by various energy conservation measures, including: minimizing heat flow from the building to the outside by insulating, and caulking; making structural changes such as installing storm doors and windows that reduce air change rates; and modifying heating and cooling systems. These indoor activities and conservation measures modify the transport and transformation effects of indoor air pollutants, thus affecting potential pollutant related health hazards. Research to identify the effects of conservation measures is essential and studies in the area of air filtration are underway.

Summary of Research Needs

The following is a brief summary of transport and transformation research needs that would provide clarification and detailed information.

Effects

Atmospheric Pollution

- o Development of atmospheric models to study transport mechanisms and the fate of oil- and gas-generated emissions in the immediate vicinity of and downwind from sources. These should be specific to oil or gas and focus on fugitive emissions.
- o Assessment of oil- and gas-generated air pollutants and their behavior relevant to other sources that contribute to total loading. This is important since there will be similar emissions from synthetic fuel facilities and synfuel combustion.
- o Development of mathematical reaction models to study ethylene levels in urban areas with increasing traffic density and the rate of reaction product formation (in this era of catalytic converter use) (e.g., perchloroethylene, ethylene dichloride, and ethylene dibromide).
- o Collection of data relevant to the photocatalytic processes that can convert innocuous hydrocarbons into polynuclear aromatic species that would be of concern for public health.
- o Collection of data on the hydrocarbon species present in aerosol particulate matter emitted in combustion.
- o Collection of data on organometallic substances in particulate emissions that may serve as catalysts, solvation agents, or residual valence forces responsible for adsorption.
- o Identification of the changes in qualitative profiles of emissions resulting from technology and design changes, fuel conversion, etc., which may affect profiles of ambient hydrocarbon levels.
- o Utilization of tracer hydrocarbons such as acetylene to indicate the contribution of hydrocarbons from the combustion of each oil and gas product (gasoline, natural gas liquids, and fuel oils) to total nonmethane hydrocarbon concentrations.

Indoor Pollution

- o Development of models to study pollutant decay and transformation products in homes using oil- and gas-fired furnaces, stoves, and ovens.

- o Identification of products of interactions of indoor air pollutants and of the effects of temperature, humidity, air flow patterns, and number of occupants on such interactions, as well as associated health effects.
- o Study of the transport patterns of indoor and outdoor pollutants in and around the house, especially with regard to energy conservation measures such as insulation, and solar heating and cooling.
- o Design of indoor standards for NO_x , CO, SO_x , and hydrocarbons, taking into consideration oil and gas appliances.
- o Study of the potential for the indoor formation of secondary pollutants (i.e., sulfates, nitrates, oxidants, nitrosamines).
- o Study of indoor/outdoor air exchange patterns in homes and buildings as a function of structural design (e.g., high rise ceilings, multi-story stairwells).
- o Study of the cumulative effects of indoor pollutants generated from indoor activities considering sources other than oil and gas end uses (e.g., aerosol sprays, solvents, paints). This is critical to an understanding of compounding variables.

Characterization, Measurement, and Monitoring

Stationary Source Combustion

- o Characterization of fly ash particles for identifying trace metal compounds emitted from oil-fired power plants and the potential for catalytic activity on the particle surface.
- o Development under field conditions of real-time measurement of ambient volatile compounds near heavily traveled streets.
- o More extensive determination of the composition and rate of emissions functions of boiler and burner type, fuel characteristics, air/fuel ratio, and fuel load. Much EPA research already has been performed in this area, however, the need for both energy efficiency and purity of combustion requires that this become a major research thrust, especially in light of emerging indoor pollution problems in large industrial and commercial buildings.

- o Study of seasonal variations in emissions levels from distillate oil- and waste oil-fired residential and commercial heating units, especially with respect to indoor and local outdoor pollution episodes.
- o Identification of chlorinated hydrocarbons and dioxins in airborne particulates from oil-fired power plants.
- o Determination of the potential for olefin formation on particles emitted from coal-fired power plants as a result of the irradiation of absorbed hydrocarbons released from oil and gas combustion.

Mobile Emissions

- o Characterization of exhaust particles from gasoline- and diesel-powered automobiles (see text for details).
- o Development of refined methods to measure and monitor automobile exhaust constituents.
- o Assessment of interactions among exhaust constituents during collection and storage and identification of reaction products.
- o Development of standardized techniques for interpreting diesel emissions source data.*
- o Development of an ethylene monitoring system for specific geographic areas, e.g., California (Los Angeles), Colorado (Denver).
- o Identification and quantification of suspected carcinogens, nitrosamines, chlorinated dioxins, and other potentially toxic substances in gasoline and diesel exhausts.
- o Quantification of polycyclic aromatic hydrocarbons and measurement of the effects of variables on hydrocarbons emitted from light duty vehicles.

*In a recent Ford Motor Company study of emissions from diesel engines, chromatographic and mass spectrometric techniques were employed to ascertain that most of the biologically active species were oxidation products. The majority of more than 100 compounds identified were formed during sampling or storage, or during the separation process; therefore, caution is advised in interpreting all diesel emissions source data until standardized techniques are developed. The development of these techniques is a high priority.

- o Development of uniform, standardized, and quality controlled data gathering and reporting system. This is necessary to assess hazards related to oil and gas end use.
- o Characterization of diesel odor components and development of control methods and materials.
- o Development of environmentally safe substitute additives to be used in diesel and gasoline fuels such as smoke and odor suppressants and antiknock agents (see text for details).
- o Determination of hydrocarbons, organic lead vapors, and other toxic constituents of exhaust in busy garages, bus depots, and service stations.

Indoor Air Pollutants

- o Development of sensitive instruments to measure and detect low levels of indoor air pollutants generated from oil and gas appliances.
- o Measurement of evaporative hydrocarbon levels when a gas stove and oven are in use, and when only the pilot light is in operation.
- o Collection of data on the dosages of an indoor air pollutant that an individual would receive when exposed to varying concentrations for different lengths of time.
- o Comprehensive quantitative measurement of all indoor air pollutants generated from stoves, ovens, and furnaces.
- o Development of sensitive instruments and appropriate sensing methods for measuring low levels of indoor radon emissions, especially with regard to natural gas range surface burners and ovens.
- o Study of the effects of energy conservation measures on indoor pollutant levels and their residence time.
- o Development of monitoring methods to detect and collect information on indoor concentrations of nitric acid, nitrosamines, and nitrate.
- o Development of an information base and exposure inventories together with well designed field measurements for indoor air pollutants.

- o Development of reliable instruments that can continuously monitor indoor emissions over longer periods of time.
- o Development of simple, real-time detectors of the toxic indoor concentrations of pollutants.
- o Study of the frequency with which SO₂, CO, NO_x, sulfates, nitrates, and hydrocarbons occur in the indoor air.
- o Determination of chlorinated dioxins in indoor airborne particulates emitted from oil- and gas-fired appliances that could be collected on electrostatic precipitators.

Part 8

Unconventional Resources

UNCONVENTIONAL RESOURCES SUMMARY

Few health and environmental effects studies related to the various unconventional energy technologies have been performed. In this section, relevant research needs are discussed along with effects issues associated with each of the technologies.

Of overriding and critical importance with respect to these emerging technologies is the need to exchange information among researchers and project managers associated with technological development. The techniques proposed for recovering oil from U.S. tar sands are also applied to recovery of deep light oils and heavy oils, as well as enhanced recovery of oil shale by in situ techniques. Some heavy oils are produced in California and Texas by thermal methods (and are included in conventional oil reserve estimates). Gas from geopressured brines, eastern shales, western tight sands, and deep basins is expected to be extracted through the application of fracturing and use of drilling muds--methods that are also employed to recover the resources named above.

The resources discussed in this section are classified by various Federal agencies under different programs, depending upon the agency's convenience and statutory mandates, pricing categories for the resource, and definitions of conventional versus unconventional resources. As an example, research in support of heavy oil may be categorized as conventional crude oil research by one agency and as support of synthetic fuels development by another (the Energy Security Act classifies undeveloped heavy crude as a synthetic fuel). As a result, many duplicative development and research strategies are taking place. Health and environmental research would often apply to several technologies. An information transfer strategy is needed which will enable relevant generic, regional, and process-specific research to be brought to bear on solving similar oil and gas health and environmental effects problems.

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UNCONVENTIONAL RESOURCES

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UNCONVENTIONAL RESOURCES

Within this section, various new sources of oil and gas are discussed. Some of these new sources are already contributing to the domestic oil and gas supply base. These are not treated in as much depth as the conventional oil and gas industry, but are presented as examples of substantial future inputs from non-conventional sources. (Although addressed in other Committee-sponsored reports, synthetic oil and gas from coal and oil shale should be noted as new sources.) As they are developed, these new sources will probably change the character of the oil and gas industry--enhancing its diversity of resources, processes, distribution systems, and marketing patterns.

OIL

In the last 100 years, more than 450 billion barrels of oil have been discovered in the U.S; however, only about 115 billion barrels have been produced. Advances in conventional drilling and well completion technology can allow only for the production (including enhanced recovery) of another 30 billion barrels from these fields, leaving about 305 billion barrels. Another 26 billion barrels of oil are contained in Utah's tar sands; 30 billion barrels of heavy, viscous oil are located in California; and billions more are located elsewhere in shallow diatomite formations and in tar sands. Much of this oil is recoverable with new oil mining techniques. These new methods and resources are discussed in this section.

The Sources

Oil Mining

The term "oil mining" encompasses several new and innovative processes used primarily to extract thick and heavy oil. These techniques include: (1) removing oil-bearing rock through conventional mining techniques and heat extraction of the crude; (2) excavating huge pits down to the oil bearing formation and applying chemicals to loosen the oil, and (3) the excavation of a series of tunnels underlying the oil-bearing formation with holes projecting upward to allow oil to collect within the tunnels for recovery.

These processes are attractive because they apply not only to heavy crude, but also to tar sands, and to oil fields of lighter crude where conventionally recoverable supplies of crude have been exhausted. It has been estimated that oil mining can increase the economically exploitable U.S. oil reserves 10-fold. As the price of oil rises, the mining of it underground or on the surface will become economically more attractive (Smith 1979; Dick and Wimpfen 1980).

The conventional method of oil extraction by drilling is highly inefficient, leaving 40 to 60 percent of the oil in the ground, even with the use of enhanced oil recovery techniques. This efficiency of recovery is in contrast to some mineral mining operations that recover up to 90 percent of the ore. Much of the oil left behind after conventional recovery can be mined.

The concept of oil mining is not new. At Macksburg, Ohio, in 1865, a large-diameter shaft was sunk in place of the small drill hole of a well that had begun to yield a small amount of oil and much water. A small quantity of oil was then skimmed from the top of the water in the large hole. In California the following year, a series of tunnels was excavated slanting upward into a natural oil seep area on a mountainside. From each of 30 tunnels, between 1 and 20 barrels of oil per day were gravity fed at the tunnel mouth. These and other tunnels dug in the 1890s continued to produce oil for several decades.

In 1932 a U.S. Bureau of Mines study of oil mining feasibility concluded that the method could bring large financial returns and recover oil that would otherwise be lost in U.S. oil fields (Rice 1932).

Oil mining in Europe began in 1735 with the excavation of tunnels into an oil bearing formation in France. By the 1930s the underground tunnel network had been extended to an area covering three square miles. In Germany, oil mining began at Wietze in the late 19th century and gained some significance in World War I when a shaft 13 feet in diameter was sunk to a depth of 495 feet. Oil skimmed from this shaft totaled 127,000 barrels in 1918 (Dick and Wimpfen 1980).

Currently, oil mining is centered in Canada and the Soviet Union. In Canada, oil mining is utilized in the excavation and removal of oil from tar sands. In western Russia, where only 2 percent of the Yarega oil field could be tapped by conventional drilling and pumping, shafts were sunk to a depth of 500 feet to aid in the recovery of heavy oil. Horizontal galleries radiate from each shaft. Inclined passages extend from each gallery down into the oil-bearing formation to a production gallery as large as 80 feet in diameter. Uptilted holes radiate from each production gallery for a distance as long as 800 feet. Steam, injected into the reservoir rock from the horizontal galleries, aids in promoting the flow of the heavy oil into the collection holes. It is estimated that the combination of subsurface excavation, lateral drilling from the production galleries, and steam injection will make it possible to recover up to 60 percent of the oil in the reservoir. More than 300 other reservoirs of heavy oil in the Soviet Union are being considered for application of the oil mining technique (Dick and Wimpfen 1980).

Conoco has been operating a 50-barrel-a-day underground mining plant for the last 3 years on a shallow oil field near Casper, Wyoming. The oil is drained into a 2,000-foot-long horizontal shaft, 180 feet underground. Getty Oil Company is constructing a \$21 million pilot plant at its McKittrick field outside Backersfield. The plant is expected to produce 20,000 barrels a day by the late 1980s. The field, under a decline in production, is expected by Getty to produce 400 million barrels, largely through digging and processing the carbon-rich diatomite before the field is mined out. This production will amount to almost twice the total production from the field during the 80 years it has been tapped (Smith 1979). The processing will be performed by two methods which will be evaluated. One is a coal liquefaction process and the other utilizes a solvent proven successful in extracting vegetable oil from soybeans.

The exploitation of the tar sands of Utah, New Mexico, California, Texas, and the eastern states by the emerging U.S. tar sands industry is expected to utilize surface mining to a large extent. Researchers at the University of Utah predict that up to 150,000 barrels a day of oil can be produced from unit processes that depend upon mining tar sands (Smith 1979; see the section on tar sands below).

The Kern County, California, deposits of heavy oil are expected to be recovered, largely through oil mining techniques (see the section on heavy crude oil below).

The concept of oil mining incorporates surface mining, in situ, and underground mining. Surface strip mining is efficient for deposits at depths down to 180 feet in flat terrain. Open-pit mining is suitable for deposits with irregular surface topography and those that are deeper than 180 feet. Surface terrace mining, a variation of open-pit mining that involves outwardly spiraling strip mining, is applicable to relatively shallow deposits covering a wide area.

Underground mining is relatively inefficient for oil mining since the oil bearing rock is brought to the surface much like bituminous coal. Rock formations strong enough to be safe for tunneling have a low oil content. Conversely, when the proportion of oil to rock is high enough to make mining the oil economically attractive, the rock surrounding the tunnels is dangerously weak (Dick and Wimpfen 1980).

The most promising oil mining method is a modified in situ approach similar to that practiced in the Soviet Union. The operation requires the presence of a structurally sound rock stratum adjacent to and under the oil reservoir. Working in underlying tunnels, miners would drill and extend solid casings up through the water zone

of the reservoir to the oil zone. Thus, oil would seep through perforations in the end of the casings and drain into a collection system in the tunnels below.

Heavy Crude Oil

Heavy crude, as the name implies, is more dense than conventional crude oil. Its specific gravity is generally considered to be less than 20 degrees, compared to 34 degrees for the oil industry's standard, Saudi Arabian light crude oil (Kotkin 1979). It is more expensive to extract and difficult to refine, partly due to its high content of sulfur and other impurities. Often the oil must be heated to keep it adequately fluid.

The availability of heavy oil as a major energy source is related, in large measure, to economics. Former President Carter ordered an end to price controls on heavy crude oil in an attempt to "significantly increase production in American crude oil reserves" and consequently add to the nation's energy security (Schram 1979). This action is expected to increase the current production of heavy crude oil of 250,000 barrels a day to 450,000 by 1985 and 750,000 by 1990. One study predicts an output of 2 million barrels a day by 1985 (Braun 1979).

Most of the heavy-oil-bearing lands are in Utah and California. To date, most of California's heavy crude has been extracted near Bakersfield while a large reserve is under the city of Long Beach, California. Conservative estimates say as many as 10 billion barrels of heavy crude exist in the U.S. (Schram 1979; Braun 1979). Other estimates vary from a relatively modest 150 billion barrels in place with 30 to 45 billion barrels recoverable (Schurr et al. 1979), to enough heavy oil to allow the U.S. to be "totally independent of the Middle East in 20 years" (Braun 1979).

Huge reserves may exist outside of the U.S., perhaps in at least 60 countries. Most untapped fields are known to be in the Western Hemisphere from Alaska to the tip of South America. As much as 967 billion barrels of heavy oil--more than the total of estimated light oil reserves of the entire Persian Gulf--are expected to be found in the rich tar sand deposits of Alberta, Canada. As many as 2 trillion barrels of heavy crude may lie along the Orinoco River in Venezuela--an amount equal to the petroleum consumed by all countries of the world to date (Braun 1979; Kennedy 1979).

Most of the heavy oil found within the U.S. has been a by-product of the search for light oil. Since a systematic search specifically for heavy oil has not been made, U.S. reserves are difficult to estimate with accuracy. Exploration and development of

this resource is expected to depend primarily on anticipated profits. As long as greater financial incentives are associated with extracting and refining light oil, heavy crude is not likely to become a major source of petroleum products.

A new process to improve the recovery of heavy oil has been developed by the Hop Corporation, a subsidiary of Barber Oil Corporation. The process uses horizontal steam injection into heavy oil deposits, rather than the conventional method of drilling wells much like regular oil wells for the vertical injection of steam. The company anticipates that the technique will permit the efficient and economical production of heavy oil from reserves that have not been commercially viable (The Wall Street Journal 1979).

Project DEEPSTEAM, A Department of Energy-sponsored effort to develop methods of freeing heavy oil from reserves too deep for conventional techniques, has begun field testing near Bakersfield, California. Scientists from Sandia Laboratories at Albuquerque and from Chevron USA are testing a prototype steam generating system that could eventually enable companies to tap highly viscous oil deposits as deep as 5,000 to 6,000 feet, roughly twice the depth that is economically practical today. The key to project DEEPSTEAM is a "down-hole" steam generator. Injecting steam into a heavy oil reservoir thins the oil, making it flow more readily to nearby production wells where it can be pumped to the surface. Conventional systems, however, must first produce steam in boilers on the surface, then pipe it down the borehole. The technique is limited to depths of 2,500 feet or less; at deeper levels the steam cools too much to be effective (U.S. Department of Energy 1980a).

Using the new concept being tested by Sandia, steam would be generated at the base of the borehole in the oil bearing formation itself, rather than on the surface. This avoids the heat losses commonly encountered in piping the steam, and more of the heat can actually be used to free the oil. Lowering the steam generator into the underground formation also may hold some environmental advantages. Conventional generators burn about one barrel of oil for every three recovered, and the boilers require expensive scrubbers to keep emissions within air quality standards. Generating steam underground and injecting both its and the combustion gases into the deep reservoirs could significantly lessen the impact on air quality--while using only 2/3rds as much fuel as today's methods. Moreover, the carbon dioxide in the combustion gases is expected to help move the oil toward producing wells (U.S. Department of Energy 1980a).

In the current series of tests, the unit operates on the surface and injects steam and gases into an 800-foot-deep heavy oil reservoir in the Kern River Field. Then, by monitoring at both the injection

and production wells, investigators expect to determine how much carbon monoxide, nitrogen oxides, nitrous oxides, and sulfur dioxide (typical combustion gases) escape into the atmosphere. Also, by comparing production from these wells with past production using pure steam injection, it can be determined if the combustion by-products actually boost oil flow. The tests also will help reveal if particulates from the combustion gases might plug the oil formation and prevent steam from moving away from the injection well (U.S. Department of Energy 1980a).

Steam flooding in relatively shallow heavy oil reservoirs with high heavy oil content has been performed by the Santa Fe Energy and Getty Oil companies in California. Cyclic steam stimulation was used to reduce viscosity and improve mobility of the oil.

In situ combustion, a process similar to that utilized in the underground gasification of coal and oil shale, involves high-temperature oxidation in the heavy oil reservoir by continuous injection of air or air and water. During the process, part of the oil is converted to coke which is then consumed to produce more heat. The water is turned to steam that, in turn, distills some of the oil in advance of the reaction, causing it to become more mobile and to move readily toward producing wells. Field testing of in situ combustion of heavy oil has been conducted by the Husky Oil Company in California without success and by the Cities Services Oil Company in Louisiana, where increases in production have been obtained and where new variations in operation are being tested (U.S. Department of Energy 1980b).

Tar Sands

Tar sands are characterized by hydrocarbon bearing deposits of rock whose interstices contain highly viscous to semi-solid bitumen (mineral pitch) or crude oil with mobility insufficient for adequate movement to a wellbore. In tar sand, the bitumen is so viscous and immobile that it prevents displacement and production by conventional recovery methods. Generally, tar sand oils have specific gravities of less than 12 degrees, compared to about 15 to 20 degrees for heavy oil and 34 degrees for Saudi Arabian light crude oil.

Within the U.S., most tar sands are in Utah. Until recently they had been regarded as too remote and inaccessible for recovery to be economically viable. In North America, the largest reserves of tar sands cover about 12,000 square miles of northwestern Alberta, Canada. These deposits are variously estimated to contain at least 900 billion barrels of oil--more than the world's proven conventional reserves and enough to supply North America's oil demand for over 100 years. Currently, Canada extracts about 90,000 barrels of oil a year

from the deposits. In 1978 a joint venture of four oil companies and the government of Canada was formed to initiate a project designed to produce 125,000 barrels of oil a day from the tar sands by 1982. Because most of the sands are deep (200 feet or more below the surface), only about 25 percent of the oil is recoverable with conventional technology (Canada Today 1979; Time 1979).

In Canada, bucket-wheel excavators are used to remove the sands from shallow deposits to 150-ton trucks that carry the material to processing facilities. The tar is then separated from the sand by heating with hot water, producing a "contaminated asphalt" that is run through a coking and hydrosulfurization process to produce synthetic crude oil. By-products of the process are coke and sulfur.

Of 500 U.S. tar sand deposits identified in 22 states, only 39 have been meaningfully assessed in terms of resource size. These have been estimated to contain up to 30 billion barrels of oil in place (about equivalent in size to current estimates of conventional petroleum reserves), of which 29.3 billion barrels are estimated to be located in 27 deposits within the state of Utah (U.S. Department of Energy 1980b; Resources for the Future 1979).

So far, U.S. recovery has focused on small-scale mining of shallow surface deposits to produce tar sand for direct use in road paving. Most of the U.S. deposits lie under overburden material that is too thick for economical surface mining, so in situ recovery will be required. Steam or hot water injection and in situ combustion are the two processes considered for the release of bitumen from deep U.S. tar sand deposits.

Because of the abundance of accessible surface deposits in Alberta, little experience has been gained in the underground recovery of oil from tar sands. Conventional hardrock mining is not feasible due to the structural character of tar sand deposits. However, it may be possible to utilize modified conventional longwall mining techniques to recover tar sands.

Hydraulic mining, a technique proven successful for the underground mining of uranium ore, may be feasible and recently has been tested with tar sands in southern California. In this process, a capsule containing a high pressure nozzle, a slurry pump, and piping is lowered through a casing into a shaft drilled through the tar sands zone into the underlying formation. The nozzle directs a stream of water against the tar sands deposit, breaking the material into small pieces which are then entrained in the wastewater as a slurry. The slurry drains into the sump in the underlying zone and from there it is pumped to the surface for aboveground processing (Tetra Tech 1977).

Although attractive from the standpoint of not requiring huge capital investments for aboveground retorting and separation facilities, from a technical standpoint in situ recovery is a much more complex operation than aboveground processing. Essentially, in situ recovery techniques completely process the tar sands underground, removing only the valuable bitumen and leaving the sand matrix in place. But when these reactions take place far underground, monitoring and controlling become monumental tasks. Even though handling of sand is eliminated, large quantities of recovery fluids must be pumped. Because recovery rates depend on many unknown natural geologic characteristics, recovery efficiencies are usually much lower than those attainable aboveground where such conditions may be controlled. Thus, overall, in situ processing is unlikely to be any less expensive per unit of oil recovered than aboveground processing, but where deep deposits exist, it is the only recovery technique that can be used (Tetra Tech 1977).

Thermal stimulation has been used by the conventional oil industry for many years for secondary and tertiary recovery in depleted oil reservoirs. The primary difference in tar sands applications is that the low gravity and high viscosity of bitumen require extremely high displacement pressures to initiate flow. Such processes are limited to deep deposits that have enough overburden to contain the high pressures (Tetra Tech 1977).

Cyclic steam injection is a technique developed in Alberta in which steam is injected into tar sands strata and oil is produced from the same well. As steam is injected, it lowers the viscosity of the bitumen around the well, thereby increasing the permeability. This increased permeability then allows the less viscous bitumen to be removed from the well. Continued injection cycles expand the halo of permeability around each well until the halos of adjacent wells overlap and conventional steam flood may be used.

In a formation with communication established between adjacent wells, the steam flood process may be used. Steam injected at one well site forces bitumen ahead of it toward a production well. This process has been studied by Shell Canada at its Peace River test site. Rather than using cyclic steam injection to achieve communication between wells, however, Shell used a steam soak process in which steam was constantly injected until breakthrough. This breakthrough required 2 years in a tar sands zone about 2,000 feet deep. While maintaining steam injection, backpressure was increased over a 6-month period until the desired pressure of about 1,000 psi was obtained. Next, the steam pressure was maintained for about 1-1/2 years until the entire zone was heated; then the pressure was lowered to about 250 to 500 psi for a production period of about 1-1/2

years. Shell officials said this process was developed for use specifically in the geology in the Peace River deposit and would have to be changed if different geological conditions were encountered (Tetra Tech 1977).

In the early 1960s, Shell Canada conducted tar sands recovery tests based on injection of steam and sodium hydroxide. The tests indicated that horizontal fractures can be induced in tar sands to establish communication between injection and production wells. Once these fractures are formed, emulsifying fluids can be introduced. According to Shell, 50 to 70 percent of the bitumen in place can be extracted with less than three barrels of water injected per barrel of bitumen produced.

A modified steam or hot water technique involves the use of solvent extraction. Unlike kerogen, the hydrocarbon constituent in oil shale, the bitumen in tar sands is soluble in a variety of organic solvents. This property, along with the relatively high permeability of some zones, allows tar sands deposits to be tapped by in situ solvent extraction processes. However, because solvents are usually valuable products in themselves, the loss of relatively small amounts of these materials in the waste sand can offset the gains of recovering large quantities of raw bitumen. For this reason, the solvent recovery step is the key to the economic success of any solvent extraction process.

In in situ solvent extraction processes, a solvent fluid is circulated through the impregnated zone. As bitumen is dissolved into the solvent, it is pumped to the surface. The permeability of the bitumen-free sand matrix then increases, providing passageways through which the solvent can flow to attack new areas of bitumen. Variations on this basic procedure may require heating the solvent or fracturing the impregnated zone. Two of the many processes that have been devised for solvent extraction of tar sands were patented by Texaco. In the first process, two wells are drilled into the base of the tar sands zone, one an injection well and the other a production well. Communication between wells is established by fracturing. Hot water or steam is then injected and allowed to flow between the wells. A solvent such as carbon disulfide (CS_2) is then injected along with the heating fluid. Since the boiling point of the CS_2 is lower than the temperature of the heating fluid, the CS_2 becomes vapor upon entering the impregnated zone, and diffuses into the tar sands zone, dissolving the bitumen. Once its temperature has been lowered the CS_2 condenses. As it drains back into the stream of heating fluid, it carries quantities of dissolved bitumen with it (Tetra Tech 1977).

In another process patented by Texaco, both surface mining and solvent extraction operations are used. After the overburden layer has been stripped off the tar sands zone, the pit is filled with water. Then carbon disulfide is injected into the tar sands zone immediately below the water. Carbon disulfide is used because it does not react with water and its density is greater than that of water. As the solvent removes the bitumen from the sand matrix, the water from the pit above replaces it. More CS₂ is injected and it contacts deeper levels of bitumen-rich sand. As the water level of the pond drops, more water is added to keep the cavity full. Once the bitumen has been removed, the cavity is pumped dry (except for the water remaining in the sand) and the pit is backfilled to minimize environmental damage (Tetra Tech 1977).

With respect to in situ combustion in the process of forward combustion, some of the tar sands deposit is burned to recover the hydrocarbon product from the remainder. Combustion is started in the tar sands zone near the injection well and is maintained through continued injection of air. At first, bitumen is consumed in the combustion process, but as the ore ahead of the combustion zone becomes heated, the bitumen will be driven toward the production well, leaving behind carbon residue and heavy ends as a fuel source for the combustion process. This process depends on the natural permeability of the deposit to enable the vapors produced to be recovered at the production well. If this natural permeability is not adequate, it may be necessary to fracture the zone before ignition. Regardless of the source of permeability, either natural or induced, it is vital that it be uniform throughout the vertical extent of the zone. If permeability is greater in one horizontal plane than another, the air injected will tend to create a path through that zone, causing the combustion front to finger into the path rather than to progress uniformly through the zone. Another problem with forward combustion is the plugging of pores as the hydrocarbon vapors pass through the cooler parts of the tar sands zone on the way to the production well. Even if the initial permeability of the zone were adequate to allow for the flow of vapors, condensing vapors might well plug these pathways and cause production to stop (Tetra Tech 1977).

Reverse combustion is based on the same concept as forward combustion, except the combustion zone progresses from the production well to the injection well. Because the hydrocarbon vapors that are produced pass through a heated area on their way to the production well, plugging is minimized. Furthermore, because of the high temperatures which the vapors encounter on the way to the production well, some thermal cracking occurs, leading to the production of an upgraded product.

A combination of in situ combustion and water injection processes have been tested in Canada. The first step in the process was fracturing the formation to achieve communication between injection and production wells. Forward combustion was then started and maintained. After an initial heating period, water was injected along with the combustion air. As water vaporized in the combustion zone it diffused to the surrounding tar sands and heated them to approximately 200°F (93°C). At this temperature, the bitumen was less viscous and could be moved by the air-water drive to a production well. Tests indicated that, if mechanical problems had not been encountered, recovery of in-place bitumen would have been close to 50 percent (Tetra Tech 1977).

Health and Environmental Issues and Research Needs

Oil Mining

Safety hazards common to all underground mining (coal and ore extraction) also apply to the excavation, maintenance, and use of shafts, tunnels, galleries, and drill holes associated with oil mining. In addition, with oil mining the potential for oil hydrocarbon and gas leakage poses the risk of fires and explosions. The potential for flooding from the overlying water zones also exists. Moreover, the workforce can suffer dermal and inhalation exposure to the toxic components of crude oil.

Environmental issues center on four main areas of concern: the land disturbance, reclamation, and leaching associated with storage and disposal of overburden and mine wastes; disposal of spent solvents and other process chemicals; subsidence; and groundwater contamination from in situ leaching and surface leaching from solid wastes. Most water produced as a result of the process can be reinjected into the oil reservoir.

Although surface mining is generally safer than modified in situ mining, its environmental impact may be greater. Methane gas, hydrogen sulfide, other gases, dust, and noxious odors may be expected near the mines. Overburden and tailings may impair scenic vistas while causing substantial disposal problems.

Currently, the Bureau of Mines of the U.S. Department of Interior is undertaking a detailed study intended to identify and quantify the environmental problems associated with oil mining and to identify control and abatement actions (Dick and Wimpfen 1980).

Heavy Crude Oil

Health and environmental issues associated with the extraction of heavy oils focus on mine-assisted steam flooding. The issues relate to occupational health and safety, degradation of air and water quality, and on water availability (U.S. Department of Energy 1979a).

Occupational health and safety concerns relate to the potential danger of fire and explosions associated with methane and hydrocarbon vapors; exposure to asphyxiating gases such as sulfur and nitrogen oxides, hydrogen sulfide, and carbon monoxide; dermal and inhalation exposure to toxic components in the oils and process chemicals; dangerous high temperature and pressure operating conditions; noise; and transportation accidents.

Air quality concerns relate to emissions of sulfur and nitrogen oxides and particulate matter from the operation of direct-fired boilers used in steam production. The venting of hydrogen sulfide is also a concern. The U.S. Department of Energy is conducting a study to determine the feasibility of reinjecting combustion gases with the steam as a mitigating measure to reduce air pollution.

Water quality concerns relate to the contamination of surface waters or aquifers by stored saline water accumulated during the extraction process and by toluene which is used in connection with the steam injection process. After storage, most wastewater is reinjected. The steam flooding process requires large amounts of water and its withdrawal from the surface waters in the semi-arid areas of the western U.S. may pose a severe impact on the maintenance of natural stream biota and on the amount of water available for domestic and industrial use.

With regard to occupational safety and health, bioassays are needed, along with dose-response studies, and specific safe handling procedures for the chemicals used in the various technologies. Research areas under study include developing screening tests for hydrocarbon carcinogenicity and mutagenicity, analysis of molecular processes involved in the carcinogenic action of polycyclic aromatic hydrocarbons, and evaluation of the influence of inhaling acid aerosols and particulate matter.

The major problem with mine-assisted steam flooding will be safely drilling horizontal wells from the mine shafts, and little experience is available in this area. Insufficient sand control could result in well plugging. Mining the horizontal shafts through oil and water zones also will be difficult and may require

modification of existing technology or development of entirely new methods for shaft sinking under these conditions (U.S. Department of Energy 1979a).

With regard to environmental issues, research needed in the air quality area includes improved air-monitoring procedures, evaluation of air quality near facilities, and development of improved atmospheric transport models to predict fate and dose to man and the ecosystem. Work is in progress to develop remote and in situ instruments that will detect toxic substances, suspended particulate matter, carcinogenic vapors in ambient atmospheres, polycyclic hydrocarbons, and other organic pollutants. Needed research efforts in the water quality area include examination of environmental control technology for improved brine control, improved characterization of aqueous effluents from oil refining sources, study of the biodegradation of chemical compounds discharged from refineries, and study of the effects of mixed petroleum hydrocarbons on marine fish. Some of this research is being initiated (U.S. Department of Energy 1979a).

Tar Sands

About 2.2 tons of tar sands must be mined and heated in above-ground retorts to yield one barrel of thick bitumen which can be refined by conventional technology into oil. In Canada, the cold (-4°F) winter temperatures make year-round operations difficult and the expansion of the volume of the sand (brought about by expansion of void volume) during extraction creates an environmental disposal problem. However, from an environmental standpoint in the U.S., in situ techniques have many drawbacks. (Because only 10 percent of U.S. tar sands are recoverable by surface mining, in situ techniques or underground mining methods must be developed to allow tar sands to become an important energy source.) Removal of bitumen can cause surface subsidence and carcinogenic combustion products can leach into groundwater and pollute water supplies. The disposal of waste sand containing mineral hydrocarbons and spent process solvents may cause serious environmental problems.

Air emissions of sulfur oxides occur from steam boilers and sulfur removal equipment. Hydrocarbons can be emitted from storage tanks required for the tar sand oil feed, the naptha and gas oil intermediates, products, blowdown systems, process drains, cooling towers, and leakage from valves, flanges, and seals. Particulate matter can be emitted from coke and steam plants. Nitrogen oxides also can be emitted from steam boilers. It is envisioned that facilities used to upgrade tar sand oil would pose environmental impacts similar to those associated with the coking and hydrotreating processes of an oil refinery. From the viewpoint of resource utilization, production by surface mining methods (where economically and

technically feasible) is preferred. However, from an environmental point of view, even in light of the aforementioned impacts, in situ production of tar sands is preferred by some scientists (Frazier et al. 1976).

Research needs related to an emerging U.S. tar sands industry are many and diverse. They are similar in many ways to those for in situ coal and oil shale processes, recovery of crude from new heavy oil deposits, and enhanced oil recovery techniques applied to depleting or abandoned oil wells. The reader is referred to other reports of the Interagency Committee for a listing of research needs related to emerging synfuel technologies. The major thrust of tar sands research should be utilizing information gained from researching these other technologies. This creates a need to transfer information, which is the subject of the following section.

Information Transfer

As mentioned above, all of the techniques proposed to recover oil from U.S. tar sands are also used in the recovery of deep light oils and heavy oils, the enhanced recovery of oil from old fields, and the recovery of liquids from coal and oil by in situ techniques. Some heavy oils are produced in California and Texas by thermal methods (and are included in conventional oil reserve estimates). Extraction of heavy oils is expected to accelerate through some kind of an enhanced oil recovery method (perhaps by adopting successful in situ combustion or steam injection techniques). These techniques are also expected to be utilized for U.S. tar sands and in situ recovery is a major component of the process for developing synthetic fuels from coal and oil shale.

These resources are classified by various Federal agencies under different programs depending upon the agency's convenience, mandates, pricing categories for the resource(s), and its definition of conventional versus unconventional resources. As a result, in one case heavy oils may be treated as a conventional crude oil resource or as a synthetic fuel (Energy Security Act, PL 96-294). Petroleum substitutes and chemical feedstocks produced from the chemical and physical transformation of coal, shale, and tar sands are defined as synthetic fuels. These energy resources are treated under separate programs within and among different agencies. As a result, many duplicative development and research strategies are taking place. In terms of health and environmental research, much is applicable across the technologies, especially with regard to generic and region-specific research.

An information transfer strategy is needed that will enable common health and environmental effects problems and related research

needs to be realized. Such a category would bring appropriate and available information to bear upon newly developing resources, while at the same time improving research efficiency and eliminating duplication of effort.

GAS

Reserves of unconventional sources of gas are largely so ill-defined that their true potential is unknown. These will need to be explored for, defined, and developed much like commercial deposits of oil and gas. In the U.S., large resources of methane are known to exist in Devonian shales, coal seams, tight gas formations in various parts of the country (particularly in the West), and in geopressured brines along the Gulf Coast.

There is some commercial gas production from Devonian shales (0.1 Tcf per year) and tight sand formations (1 Tcf per year). Recently, considerable attention has been paid to potentially large gas reserves in deep sedimentary basins. There is uncertainty concerning both the size of the resource in place and the potential supply-price curve for methane from each type of deposit. Industry has regarded these resources as high-risk compared to conventional oil and gas reserves. However, it is now believed that considerable quantities of unconventional methane could be obtained at a lower cost than methane produced from coal or imported liquefied natural gas (Resources for the Future 1979; Booz-Allen & Hamilton 1979).

For these reasons, these potential new sources of gas are briefly discussed below. As a result of the lack of attention paid to the development of these resources in the past, there is little understanding of the health and environmental issues and research needs associated with these potential new sources of gas.

The Sources

Methane-Saturated Brines

It is generally recognized that a vast amount of natural gas is dissolved in the underground water, both onshore and offshore, of the sedimentary basin paralleling the coasts of Texas, Louisiana, Mississippi, Alabama, and the Florida panhandle. Much of this is in hydrostatic-pressurized (hydropressured) water in an abundance that has long been recognized. The amount in the deeper geopressurized water* is largely unknown. Estimates of the amount of natural gas dissolved in waters of the Gulf and in sandstone and shale sediments along the Coast range from 4 to 60 quadrillion cubic feet (Hocott 1979; Hodgson 1978).

*With geopressurized water, the pressure of surrounding rock from below is greater than that of the hydrostatic head.

Since this area has been heavily drilled for conventional oil and gas, work has focused on mapping to define the most promising areas for methane recovery, and on identifying sand thickness, porosity (permeability), temperature, and dissolved methane content. Energy development of the geopressured waters has focused on the production of electricity, with methane recovery being a by-product. This emphasis has led to controversy in terms of priorities. That is, some scientists believe that much more energy can be acquired by placing emphasis on methane recovery without restricting pressure release to drive turbines. (A substantial drop in reservoir pressure would release large amounts of dissolved gas to accumulate in an underground gas cap) (Adams 1979; Hodgson 1978).

Although, as much as 60 quadrillion cubic feet are estimated to exist in solution along the Gulf Coast, about 90 percent may be in shale strata having permeability too low for production. Thus, the actual resource may be about 6 quadrillion cubic feet. If only 5 percent of brine and dissolved gas in place can be produced before natural flow ceases (not including gas cap pumping), only about 300 trillion cubic feet may be producible without excessive pumping costs. It has been estimated (subjectively) that 10 percent of methane-saturated brine is in sandstone reservoirs large enough to recover drilling costs. Thus, no more than 30 trillion cubic feet may be economically recoverable (still a sizeable amount) (Randolph 1979).

Eastern Gas Shales (Devonian Shales)

U.S. gas contained in Devonian and some Mississippian shales is mostly in the East, in an area bounded on the north by a line between Michigan and lower New York State, and on the south by northern Alabama. The amount of gas in the reserve may be about 1/2 to 1 quadrillion cubic feet--an amount over three times the proven reserves of conventional natural gas. Ten percent of the gas can be recovered by modern methods (Hodgson 1978; Resources for the Future 1979; U.S. Department of Energy 1979b).

The U.S. natural gas industry began in 1821 with a well drilled into a shale formation in Fredonia, New York. The well had a low, but constant productivity (only a few thousand cubic feet a day), and a long life (35 years)--characteristics typical of the existing 10,000 shale wells.

Because flow rates associated with conventional shale wells have been too low to make them economically attractive, Federal efforts have been directed toward developing fracture stimulation and drilling techniques to connect more gas-containing natural and induced fractures connected to the borehole. In areas of high fracture

density, liquid chemical explosives and cryogenic fracturing have been demonstrated to be improvements over conventional explosives. In areas of low fracture density, hydraulic fracturing with gelled water and sand is an improvement over explosive stimulation. Laboratory experiments have shown that mixtures of water and carbon dioxide appear to increase permeability, porosity, and surface area of the shale (termed gas fracturing). These and other experiments are aimed at developing low-cost fracturing methods and fracturing fluids. Sometimes fracturing does not work, but when it does, usually the output per well is still lower than that typically found in conventional natural gas wells (U.S. Department of Energy 1979b; Stobaugh and Yergin 1979; Technology Forecasts 1979).

Western Gas Sands (Tight Sands)

In the western U.S., there are thick layers of strongly cemented sand that have low porosity and permeability. These areas, largely in the Rocky Mountain states of Wyoming, Colorado, and Utah, are estimated to contain as much as 730 trillion cubic feet of gas-in-place. Small quantities of gas are produced in these areas, but only where natural fracturing of the sandstone occurs. About 1/4th to 1/3rd of the gas in place is expected to be economically recovered (American Gas Association 1979a; Mankin 1979; U.S. Department of Energy 1979d).

Major technological improvements in fracturing and formation definition are required before the full potential of the sands can be realized. Massive hydraulic fracturing, a large-scale application of fracturing techniques where the length of the fracture may be in thousands of feet and the height in hundreds of feet, is the most promising technique for tight sands. The technique opens and maintains (by filling with sand) artificial fractures which penetrate deep into the sandstone. This provides conduits for gas to migrate to the borehole.

Methane from Coal Seams and Mines

Methane, the major component of natural gas, is a by-product of many of the natural anaerobic digestion and metamorphic processes associated with coal formation. This methane often escaped by permeation and diffusion during the millions of years in which flora was transformed into coal. Frequently, the low permeability of strata associated with coalbeds limited the escape of the gas, causing its entrapment in high concentrations. Several studies lend support to an estimate that the recoverable quantity of methane from U.S. coal seams is 250 trillion cubic feet, an amount approximately equal to the known conventional U.S. natural gas reserves (TRW 1977). The total amount of methane in U.S. coal seams has been estimated at

700 to 1,000 trillion cubic feet at depths as great as 6,000 feet (Hodgson 1978). By tapping coal seams for methane, possibly 1 trillion cubic feet per year could be produced by 1985, the equivalent of 40 million tons of coal* (Hodgson 1978).

Several other gases are associated (although in small amounts) with methane in coal. These are hydrogen, water vapor, nitrogen, carbon dioxide, and helium. The gas content of a coal seam is primarily influenced by depth, moisture, and coal rank. Generally, at greater depths and concurrent higher pressures, a greater volume of gas is held within the coal. Moisture reduces the capacity of coal to absorb methane. Higher rank coals such as anthracite, especially with low moisture content, tend to contain higher levels of methane. The release of methane from coal is controlled largely by porosity, permeability, and gas pressure. As gas at greater depths exists under higher pressure, it is released in larger amounts in deeper mines (Iannacchione and Puglio 1979).

The extraction of methane from coal seams prior to mine development can minimize the poisonous atmosphere or explosion potential associated with a new underground coal mine. Recent experiments have shown that in-mine methane emissions can be reduced by as much as 40 percent when methane is drained from coal seams prior to coal extraction (U.S. Department of Energy 1978).

The techniques being investigated for capturing methane from coalbeds include drilling vertical or directional wells into coal seams in advance of a mine's working face, and drilling horizontal boreholes into virgin coalbeds from a central shaft. Innovative methods include using liquids to fracture seams, a process that can increase gas flow 8- to 20-fold (Hodgson 1978). Such gas removal methods substantially reduce the ventilation requirements necessary to maintain gas concentrations at a safe level and at the same time improve mining productivity by reducing the downtime caused by hazardous levels of methane. Gas withdrawal from previously mined areas may be accomplished through vertical wells that provide mixtures of gas and air. Mines in the Pittsburgh coal seam currently vent over 100 million standard cubic feet of methane each day. At present, no commercial use is being made of this resource (U.S. Department of Energy 1979d).

When cleaned, methane withdrawn from coal seams can be utilized in a variety of ways, such as direct pipeline injection, production of liquified natural gas (LNG), on-site power generation, heating,

*U.S. coal production in 1978 was about 650 million tons.

and as a petrochemical feedstock. The cleaning process includes removing sand and coal particles.

This resource holds the promise of protecting the health and safety of coal miners, while serving as a significant new source for methane (and helium if filtering devices are modified for pipeline gas). Barriers to its development, other than technology, involve constraints in the eastern U.S. where few coal companies have clear title to the gas. Since the market value of a ton of coal has been about 100 times the value of the methane contained within the coal, coal mining companies have had little interest in the gas-derived revenues relative to their primary objective of coal production. The recovery methods have not yet been sufficiently demonstrated to attract private investment. However, economics are becoming more favorable for commercial exploitation of this resource. For coal companies, recent interest in gas recovery is primarily due to the enhancement of coal production. The methane-derived revenues remain secondary in importance.

Methane can be recovered from both minable and unminable coalbeds, thus utilizing an entire coal seam as an energy resource. In addition, methane can be recovered from gob piles. The Bureau of Mines has an extensive program of research designed to identify the extent of methane in coalbeds and to develop control measures (U.S. Department of the Interior 1979, 1980). Methane gas is also recognized as a hazard and an energy resource in salt mines and other non-coal mines (lead and zinc, gold and silver, copper, iron, silicates, marble, uranium, limestone, oil, oil shale, and trona).

One drawback to methane recovery from coal seams is the accumulation of coal and sand particles in the well. The most promising recovery technique involves drilling and using a nitrogen-charged foam and sand solution to open natural underground fractures in the coal seam, allowing trapped methane to reach surface wells. This technique is essentially the same as hydraulic fracturing used for recovering methane from eastern gas shale and western gas sands.

Methane Hydrates

Methane or gas hydrates are solid, ice-like compounds in which gas molecules are trapped and bound to water molecules. Detected in the mid-1960s, the hydrates exist under cold temperature and high pressure beneath permafrost and in deep-ocean sediments. Soviet scientists estimate that a 30,000-year world supply--or 1.7 million trillion cubic feet of gas--lies trapped in the form of hydrates (American Gas Association 1979a; Hodgson 1978).

The physical chemistry of gas hydrates has been studied extensively and is well understood, in part because of the problems with gas transmission created by their formation in pipelines (see Liquefied Energy Gases and Transportation and Storage sections). A tendency exists for gas hydrates to form when conditions of low temperature and moderately high pressure are present and gas is available at saturation concentration. These conditions can be present in oceanfloor sediments at water depths of more than a few hundred meters (or even shallower in very cold water) and beneath permafrost. Formation of gas hydrates in sediments causes a radical decrease in permeability, as indicated both by laboratory studies and by attempts to produce gas in conditions where hydrates were forming (Dillon 1980).

Gas hydrate-cemented layers may be effective seals, forming gas traps in marine sediments at water depths of a few hundred to a few thousand meters. If such traps exist, they would occur at very shallow subbottom depths, only about 4/5ths of a mile (1/2 km) from the surface. However, drilling through the gas hydrate-cemented layer may require new engineering techniques to provide a seal around the casing. Exploration of such traps in the marine environment may be attempted first in the Blake Ridge area off North Carolina for three reasons: the gas hydrates seem to be well developed there, the area is controlled by the U.S., and it is near U.S. ports and markets (Dillon 1980).

Gas hydrate deposits appear to be well developed not only off North Carolina, but also off South Carolina and beneath the Beaufort Sea north of Alaska. These deposits may explain the large quantities of methane observed at hundreds of locations since 1968 by the Deep Sea Drilling Project sponsored by the National Science Foundation.

U.S. onshore development of gas hydrate reserves is likely to focus on the shallow and accessible permafrost. Such development is unlikely until after the conventional deposits of Alaskan gas are depleted. The production of deep-sea gas hydrates is dependent upon the development of new offshore drilling technology. One production technology under development is the circulation of light hydrocarbon fluids to dissolve the gas for subsequent recovery. However, the injection of saline formation waters might be a less expensive, more environmentally acceptable and effective way of decomposing gas hydrates held in potentially producible marine reservoir formations (American Gas Association 1979a; Hodgson 1978; Tiratsoo 1979).

Gas from Deep Basins

Recently, attention has focused on the potential for extensive reserves of natural gas to be discovered and extracted from relatively extreme depths in the earth's crust, as measured by traditional drilling practices. Within the U.S., as much as 360 trillion cubic feet of natural gas may occur below 25,000 feet in the Anadarko Basin of western Oklahoma. This basin, where more than 30 successful deep wells exist (two of them below 30,000 feet), has 22,000 cubic miles of sediments below 15,000 feet, with only 1 percent of it explored. Other deep reserves may lie in the Permian and Delaware Basins in Texas, the Appalachian Basin in the East; the Mississippi Embayment in the South; and the Arkoma Basin in Oklahoma and Arkansas (Mankin 1979; Hodgson 1978).

Drilling a well today in the Anadarko Basin, similar to those completed to depths of 30,050 and 31,441 feet a few years ago, would cost about \$10 million in 1979 dollars. Although this cost may seem high, it is far lower than the initial capital investment required for a synthetic fuel facility, particularly a coal gasification plant. One deep well completed in May 1978 produces 20 million cubic feet of gas a day. A proposed coal gasification plant in Mercer County, North Dakota, is expected to cost \$1 billion and would produce 125 million cubic feet of high-Btu coal gas daily. A similar investment in the development of deep gas could yield over 2 billion cubic feet of gas a day (Rothberg et al. 1979; U.S. Senate 1979; Hodgson 1978).

With expenditures of about \$16 billion, gas from deep basins could supply a trillion cubic feet by 1982 and as much as 4 trillion cubic feet of gas to U.S. markets by 1991. (To place these quantities in perspective, in 1978 total U.S. natural gas production was about 20 trillion cubic feet.) Such expectations indicate that development of this resource would be highly profitable (MacDonald 1979; Hodgson 1978). Technological problems that are being overcome include extremely high pressures (as great as 19,000 psi), which crush ordinary well casings, and supercorrosive hydrogen sulfide.

Tapping gas at depths below 30,000 feet may provide deep-earth gas believed to be of nonbiological origin. Such gas, normally released in volcanic emissions, consists of water, carbon dioxide, carbon monoxide, methane, ammonia, molecular hydrogen, hydrogen sulfide, and other gases. Some methane may be oxidized to carbon dioxide as it reaches the surface through hot volcanic lava at low pressure. Deep gas methane can enter the atmosphere through cold faults, mainly during earthquakes. The phenomena of flames shooting out of the ground, "earthquake lights," fierce bubbling in bodies of

water, sulfurous air, and loud explosive and hissing sounds associated with earthquakes are probably attributable to the release of methane and hydrogen (Gold and Soter 1980).

Gas from Biomass

In the broadest sense, biomass includes all living plant material and associated wastes, residues, and by-products. These can be converted into solid, liquid, and gaseous fuels. Dry biomass (i.e., ready to burn) includes logs, twigs, dry straw, and the stumps of trees. Wet biomass (i.e., at least 50 percent moisture), such as manure and municipal garbage, also can be burned, but together with wetted dry biomass it can be made to produce methane gas.

Renewable sources of marine or land biomass or organic and municipal wastes can be converted to gaseous fuels using either thermal decomposition (creating a synthetic fuel) or by anaerobic digestion, i.e., the biological breakdown of organic matter into methane (and other materials) by bacterial action in the absence of oxygen.

Biogas production techniques are many and diverse. Several utilize anaerobic digesters. The natural, oxygen-free fermentation of manure produces a burnable gaseous mixture that is 60 percent methane and 40 percent carbon dioxide. Water effluents from such a process contain nitrogen which can be used as a fertilizer.

The technology for producing gas from biomass has existed for many years and holds a great potential for future development, with possible techniques including the recovery of methane from landfills (Ham et al. 1979; Industrial Research/Development 1979). How great a contribution biomass will make as an energy resource depends on the extent to which technology will increase its productive potential. Cropland, with its high yield potential, would have to account for more than 50 percent of the output. Thus, emphasis is on improving biomass yield through such means as higher biomass-yielding food and feed crops and on recovering energy from food and fiber after it has been put to its primary use, i.e., energy recovery from sewage, manure, and urban solid wastes (Yeck 1979).

Health and Environmental Issues and Research Needs

Methane-Saturated Brines

Most of the projected health and environmental impacts associated with the development of geopressured-geothermal energy are expected to occur with development of the Gulf Coast pressured brines. These include potential impacts on land by surface modifications (construction of wells, pipelines, and power plants), subsidence, and

seismic activity. In some cases, the water discharge may be of low salinity and usable as an agricultural water supply. In most instances, disposal of such a large volume of saline water will require reinjection, canaling to a saline body of water, or reinjection to a low pressure area. Ammonia, boron, dissolved solids, and trace elements such as manganese and iron may be released in aqueous aerosols. The key environmental issues are possible land subsidence caused by high volume brine production, and possible tectonic activity and man-induced minor earth tremors caused by the withdrawal or reinjection of brines. Occupational health and safety issues relate to worker exposure to potentially hazardous substances, such as hydrogen sulfide (although more prevalent with hydrothermal energy recovery) and process chemicals, and to noise and accidental blow-outs. All significant impacts are expected to be localized in the immediate vicinity of a wellhead and processing facility (Nguyen et al. 1980; Wilson et al. 1977).

Additional research is needed on the chemistry of geopressured and hydropressured waters. To date, only a few wells have been sampled; however, enough is known to suspect that high concentrations of trace metals and other pollutants are not ubiquitous.

Since the source of the rocks surrounding the saline reservoirs is sedimentary, there is reason to believe that radioactivity may be a problem in waste materials and pipeline quality gas. Radon emissions in the home resulting from the natural gas combustion are now recognized as a serious problem warranting substantial research. (See the discussion of indoor air pollution in the End Use section.) Radioactive emissions associated with the combustion of geopressurized gas could compound an existing health hazard.

It should be noted that potential pollutants associated with drilling oil and gas wells also would be present (see Onshore section). These include residual sludges from air and water treatment, scale, cuttings, and drilling muds. The transfer of information from research on the health and environmental effects related to conventional oil and gas drilling is needed. This also holds true for transferring information from research on health and environmental problems associated with the development of geothermal energy.

Since geopressured reservoirs are more susceptible to subsidence than hydrothermal reservoirs, subsidence monitoring methods, including guidelines for field data acquisition and analysis, should be refined for use in Gulf Coast areas subject to the extraction of methane-saturated brines.

Negligible research has been conducted on the impact of methane-saturated brines and reinjection on the hydrological alteration of hot springs and other areas of freshwater upwelling in the Gulf Coast region. Many of these springs are prime recreational areas and tourist attractions that support unique populations of flora and fauna. The impact upon these ecologically and socially significant areas caused by the extraction of methane-saturated brines should be determined.

Eastern Gas Shales (Devonian Shales)

Environmental concerns related to the development of eastern gas shales include: the land use and biotic habitat impacts associated with the siting and construction of gathering lines and larger long-distance pipelines and roads; pollution of underground and surface waters due to hydraulic fracturing operations and residues from chemical explosions; and high water withdrawal rates from aquifers and surface waters. Occupational safety concerns focus on the accidental mixing or improper handling of explosives. Concern for public health focuses on contamination of the gas from by-products of chemical explosions and residues of hydraulic fracturing. In addition, potential air pollution from diesel engines and turbines required in hydraulic fracturing can result in the release of large amounts of nitrogen oxides and particulate matter (U.S. Department of Energy 1979a).

Essentially all of the above concerns are being addressed by current research (U.S. Department of Energy 1979c). One concern not addressed, but of importance to public health (see Indoor Air Pollution in the End Use section) is contamination of natural gas by radon and other radioactive materials. Some gas shales can have an average uranium concentration of 60 parts per million. When these shales are fractured, radon can be released, resulting in the enhancement of naturally occurring radioactivity and contamination of pipeline gas. Research is required to assess the nature and extent of radioactive materials in shale deposits and possible strategies to minimize the transmittal of such materials in pipeline gas.

Western Gas Sands (Tight Sands)

Health and environmental concerns related to the development of western gas sands are essentially the same as those associated with eastern gas shales. Only the severity of impact may be different. The siting and construction of extensive support networks of new pipelines to transport gas over semi-arid areas and water availability are major issues particularly associated with the development of western tight sands. Research needs are also the same as those for eastern gas shales.

Oil shale development is planned for many of the same geographical areas where western tight sands may be expected (e.g., Green River Formation, Piceance Basin, Uinta Basin). Consequently, the information data base being amassed in relation to oil shale development should actively be made available and there should be coordination of research efforts on health and environmental problems related to the two technologies. In addition, since tight sands are sedimentary in origin, the gas from these formations should be screened for radioactive materials.

Methane from Coal Seams and Mines

Many coal seams contain substantial amounts of methane that are released continuously or sporadically, often with catastrophic results, during mining. The gas is a major safety problem and its removal and use prior to mining would decrease worker mortality and injury, while at the same time increasing the size of the energy resource base.

Methane can be withdrawn from many different mines (see description of the resource) to minimize the probability of explosion and provide an energy resource. The health and environmental issues and research needs associated with recovering methane from eastern gas shales and western gas sands also are essentially applicable to the recovery of methane from coal seams and other sedimentary deposits. Since recovery often involves draining existing mines, or draining methane in front of a working face, the control of the level of methane in the work atmosphere is important to assure that workers are safe from the risk of explosions.

Recently, five men were killed in a methane gas mine explosion that tragically underscored the need for reliable methods of forecasting methane hazards in mines and other areas where workers are exposed to methane. The explosion occurred on June 9, 1979, in a Louisiana salt mine. As a result of this explosion, the mine and three other salt mines have been reclassified as gassy by the Mine Safety and Health Administration (MEAS) (U.S. Department of the Interior 1979, 8392).

The methane concentration in the return air in the mine was 90 ppm. Currently, a 100-ppm concentration is recommended by the Bureau of Mines as a simple and convenient guideline for forecasting the methane hazard in a mine, whether or not the mine is classified as gassy (a classification requiring compliance with stringent safety standards--see Code of Federal Regulations, 30 CFR 57.21-1).

The information and reclassifications that resulted from the explosion suggest that a guideline of about 70 ppm may be more appropriate (U.S. Department of the Interior 1979, 8392). New assessments are needed to establish the most appropriate concentration for a guideline.

Methane Hydrates

Studies of health and environmental issues associated with the development of gas hydrates have not taken place, nor have the issues themselves been defined. Even studies related to the nature and extent of the resource are few in number (American Gas Association 1979b).

One mechanism for recovering hydrate gas would be tapping a free-gas zone underlying a hydrate layer, but this may cause a problem. The produced free gas would cause a pressure drop that would cause the hydrates to melt, perhaps leading to melting of the permafrost which could cause frost heaves, permafrost instability, and creation of surface cracks and fissures. Once started, such discontinuities can propagate in an uncontrolled manner. This problem should be studied in detail before test wells are drilled.

Gas from Deep Basins

Considerable research is needed in the fundamental field of geophysics and geochemistry, especially with respect to deep gas reservoirs. An incidental benefit of such research may be finding new approaches to earthquake prediction. Other than the potential for catastrophic releases of hydrogen sulfide and the creation of a channel for the exit of hot fluids, few health and environmental concerns can be identified prior to a more defined characterization of the resource potential.

Gas from Biomass

Sludge remaining after anaerobic digestion is separated into a liquid effluent and solid waste material. Both are potentially dangerous if not carefully treated. The liquid effluent contains toxic materials, disease organisms, suspended solids, and undigested organic material. The suspended solids can increase the turbidity of surface waters, while the leachate from digested solids used in landfill can cause additional ground and surface water pollution. The solids contain unknown quantities of toxic chemicals, such as pesticides and trace metals, as well as pathogenic microorganisms. The large amounts of water required for anaerobic digestion could aggravate water shortages in areas already experiencing a shortage of water (Energy Research and Development Administration 1977).

The potential contamination of soils and water sources can adversely impact plant and animal life. Bacteria remaining in the water after digestion would grow, depleting the oxygen supply and adversely impacting aquatic life. Increased turbidity of streams would interfere with photosynthesis and could also be harmful to aquatic biota. The possible biological contamination of soils and water sources could create serious health hazards for humans.

Environmental impacts resulting from increased employment and resultant immigration are similar to those described above. Concomitant social and economic impacts are well known, but mitigative measures are not well understood.

The various potential environmental impacts mentioned above suggest fruitful areas for research. In addition, a coordinated and cooperative information transfer program should be initiated which will exchange health and environmental data among various processes. Currently, processes for producing methane by anaerobic digestion operate on a small scale and use a variety of biomass sources (e.g., manure, urban refuse, logging and wood manufacturing residues, agricultural crops and food wastes, industrial wastes, municipal sewage, and solid wastes).

Part 9

Basic Effects Issues

BASIC EFFECTS SUMMARY

Broad issues and research needs related to many facets of the oil and gas industry are discussed in this section, including hydrocarbons. These are in the nature of basic research. A basic research theme that is not addressed in this section is treated in depth in other sections of this report. This theme is the need for increased research emphasis on the characterization, monitoring, and chemistry of hydrocarbons of significant health concern that are in the ambient environment, such as polynuclear aromatic hydrocarbons and amines. Attention should focus on the Gulf Coast, Southern California, northeastern industrialized areas, and other industrialized regions to utilize the available research resources effectively.

With respect to basic research, naturally occurring atmospheric hydrocarbons are derived from many sources, but their effects are not well understood and presumably may be beneficial due to the adaptability of biotic organisms. This warrants further study. To characterize atmospheric hydrocarbons, a more accurate and reliable replacement for the flame-ionization detector is needed. A nationally coordinated methane monitoring program is needed to provide data for a number of different energy focused assessment studies. Also within this section, the broad subject of the role of hydrocarbons in the atmosphere is discussed. This discussion provides background information for many sections of the report.

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BASIC EFFECTS ISSUES

The following discussion covers a few health and environmental effects issues related to many facets of the oil and gas industry. The issues discussed are not covered in detail within any of the preceding sections. Certain broad issues, relating to many facets of the industry that have been treated in depth elsewhere* are not discussed in this section. Since many of the basic effects of hydrocarbons relate to airborne emissions, a general discussion of the known role of hydrocarbons in the atmosphere is provided in an appendix to this section.

NATURAL HYDROCARBON EMISSIONS

Within the last decade the presence in the atmosphere of natural hydrocarbons, including methane, has been well documented. Although most of these hydrocarbons arise from biological sources, small and highly localized quantities of methane and other lower-molecular-weight hydrocarbons have been associated with emissions from geothermal areas, coal fields, natural gas and petroleum fields (including natural seafloor seeps), and forest and brush fires. Recently, methane of nonbiological origin, associated with the release of gases from deep in the earth's mantle during earthquake and volcanic activity, also has been identified as a natural emission.

Most of these natural hydrocarbon emissions occur during the natural decomposition of organic matter in both land and water (swamps, marshes, and sediments). Volatile terpenes and isoprenes are also a major constituent of natural hydrocarbon emissions. These compounds have been associated with plant metabolism and contribute to the blue haze of the Appalachian Mountain region. They also can play a significant role in photochemical aerosol formation.

Ambient methane concentrations appear to be uniform and ubiquitous except for localized anomalies (e.g., swampy areas, tectonic fissures). Measurements of other low-molecular-weight hydrocarbons such as ethane, ethene, ethylene, butane, terpene and isoprenes have been few in number, especially in nonurban areas. Estimates of the average life of these compounds in the atmosphere are varied and range from a few years to 20 years for methane, and on the order of

*For a discussion of the effects of hydrocarbons on humans and other biota, see the Onshore, Offshore, Refinery Operations, and Transportation and Storage sections; for the effects of evaporative emissions on air quality, see Refinery Operations, Transportation and Storage, and End Use sections; and for the effects associated with oil and gas combustion products, see the End Use section.

days to months for higher-molecular-weight hydrocarbons. About 43 percent of these emissions occur during summer (June, July, and August) and almost half occur in southern states (U.S. Department of Health, Education, and Welfare 1970; first external review draft of Facts and Issues Associated with the Need for a Hydrocarbon Criteria Document, see Federal Register, March 10, 1980; pp. 15262-15263).

The role of natural hydrocarbon emissions with respect to air quality and related biotic effects is not well understood. Some of these emissions may be beneficial owing to evolutionary adaptation of biotic mechanisms to natural emissions. If this is true, land clearing and water pollution may be responsible for decreased ambient levels of these hydrocarbons and their biotic value may be partially replaced by hydrocarbons from technological sources. This is an area where research is needed.

MEASUREMENT OF PHOTOCHEMICAL OXIDATION

Hydrocarbons react with other compounds in the atmosphere on exposure to sunlight, producing ozone and other photochemical oxidants. The chemistry of oxidants formation is described in detail by the National Academy of Sciences (1976, 1977). The description presented below is a highly simplified version of the complex chemical reactions leading to photochemical air pollution that underscores the pivotal role hydrocarbons may play in these processes.

The major photochemical oxidants--ozone (O_3), nitrogen dioxide (NO_2), and peroxyacetyl nitrate (PAN)--are secondary pollutants formed from other pollutants in the atmosphere under favorable conditions. Ozone, present in the highest concentrations, is the product of a reaction in which common diatomic oxygen (O_2) reacts with molecular oxygen (O) in the presence of a third molecule (M), where M is usually a nitrogen compound or oxygen:

The atomic oxygen (O) reactant is generated largely from the photolysis of nitrogen dioxide (NO_2):

The reaction mechanism is completed by the reaction of the two non-ozone reaction by-products to regenerate nitrogen dioxide and diatomic oxygen:

These reactions are the mechanism for atmospheric ozone formation, but alone they do not account for ozone accumulation. Photochemical hydrocarbon reactions affect the relative rates and the concentrations of reaction products. Modeling and smog-chamber simulations show significant oxidant formation when reactive hydrocarbons are present. Hydrocarbons photochemically regenerate free radicals that react with oxygen to form alkylperoxy- and hydroperoxy-free radicals. These radicals react with NO to form NO₂:

Hydrocarbons are oxidized in the process. These hydrocarbon reactions essentially "pump" the primary reaction of NO₂ photolysis by scavenging this reaction's NO product and making available more NO₂ reactant. In the process, atomic oxygen is made available for ozone and other oxidants formation. The amount of "pumping," and thus the amount of oxidants formed, depends on the concentration and reactivity of the hydrocarbons present.

Hydrocarbons are classified with respect to oxidant-related reactivities in urban atmospheres. Alkenes (olefins), benzene derivatives, and aldehydes have the highest reactivities. Methane, ethane, propane, and benzene essentially do not participate in these reactions. These reactivity data reflect rates of formation rather than resulting peak oxidant concentrations. The same reactions occur with lesser reactive hydrocarbons at a slower rate over a longer period of time.

A number of conditions affect the formation and buildup of ozone concentrations. Moist air significantly aids ozone formation. In the absence of hydrocarbons an equilibrium is established among ozone, nitric oxide, and nitrogen oxide. Concentrations of these compounds and reactive hydrocarbons change diurnally in response to available sunlight and darkness. Atmospheric particulate components, such as metal oxides and carbon particles, have a catalytic effect on many photooxidation reactions.

Besides ozone (O₃), a number of other compounds are photochemical oxidants--nitrogen dioxide (NO₂), hydrogen peroxide (H₂O₂), organic peroxides, organic hydroperoxides, and peroxyacyl nitrate. Organic peroxides have the general formula ROOR. Organic hydroperoxides have the formula ROOH. The major peroxyacyl nitrates are peroxyacetyl nitrate (PAN) and peroxybenzoyl nitrate (PBN). (Actually, this nomenclature is inappropriate for these structures--better names would be acetyl peroxyxynitrate and benzoyl peroxyxynitrate.)

The comprehensiveness of atmospheric hydrocarbon measurement data is deficient. Most available data concerns only total hydrocarbon concentrations measured by flame-ionization detectors (FID). Nonmethane hydrocarbons (NMHC) are measured by gas chromatographic separation of methane from total hydrocarbons followed by FID measurement of methane and total hydrocarbons in the air sample. NMHC data are obtained by subtracting methane from total hydrocarbon concentrations. Since the FID responds to organically bound carbon in compounds other than hydrocarbons, the measurement of NMHC may more appropriately be termed nonmethane organic compound (NMOC) measurements.

FID techniques have been associated with high measurement errors and variability. This must be kept in mind when NMHC data are compared with exposure data from toxicity studies and air quality monitoring. It is apparent that FID measurements are inadequate for the complete characterization of hydrocarbons in ambient air. There is a need for continued development and refinement of accurate, reliable field instruments for measuring NMHC--individually and collectively--in ambient air and in source emissions. For the measurement of individual compounds, emphasis should be placed on standardizing chromatographic techniques for qualitative and quantitative measurement. This is needed both for an improved understanding of atmospheric hydrocarbon chemistry and from a public risk perspective.

METHANE MONITORING

Monitoring ambient concentrations of methane is necessary to identify the resources and fugitive emissions associated with both unconventional and conventional sources of natural gas. Knowledge of the sources and sinks of methane is a central topic of interest in the research disciplines of geochemistry, ecology, and atmospheric chemistry.

The atmospheric chemistry community has speculated that the stratosphere is a sink for methane and that this sink mechanism is connected with the earth's ozone layer, which acts as a protective shield against excessive ultraviolet radiation. The oxidation of methane may contribute to a decrease in ozone levels. A smaller, but extremely important phenomenon, the oxidation of methane in the troposphere is also of great interest in the study of the photochemistry of the troposphere (Crutzen et al. 1976; Heidt and Pollock 1976).

Oceanographers and ecologists are interested in monitoring methane generated by anaerobic processes on land and in swamps, marshes, lakes, estuaries, and the ocean. Such sources of methane tend to obscure the contribution of urban pollutant plumes. Methane monitoring also can be useful in other areas, including: tracing the

flow of carbon through the ecosystem (useful to the understanding of the global CO₂ cycle); searching for natural gas sources; identifying leaks from natural gas development fields including geopressurized fields, western tight sands, deep gas, coal seams, and in situ combustion, as well as leaks from transmission lines; and identifying potential locations of earthquake activity.

A nationally coordinated atmospheric methane monitoring program is needed, covering local, regional, and global monitoring. This program could support the research needs of these various areas through the development of a common data base.

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APPENDIX

ROLE OF HYDROCARBONS IN THE ATMOSPHERE

The degree of airborne transport by petroleum pollutants is a function of both the physical and chemical characteristics of the pollutants and any other processes (e.g., atmospheric phenomena) acting upon them. It is the combination and interaction of various components within each of these two areas that determine how, and to what extent, individual or mixed pollutants are transported.

Airborne pollutants may be envisioned as consisting of two broad classes: particles and gases. These classes are not necessarily discrete, i.e., they can exhibit varying degrees of interactions both with each other, and also with other non-pollutant atmospheric constituents. In this context, airborne particles may be pollutants themselves or be non-pollutant particles on which pollutants are adsorbed. Pollutant vapors that are emitted to the atmosphere may remain unchanged, undergo complex photochemical reactions, condense on particulate matter, or form aerosols.

In the area of atmospheric particulate pollution, aerosols--especially these containing polycyclic organic matter--are of great importance from the standpoint of human health (National Research Council 1972). It is in the form of aerosols that many organic pollutants, both particulate and vaporous, are transported to and through the atmosphere. (For this discussion, an aerosol can be considered to be a gaseous suspension of ultramicroscopic particles of a liquid or solid.)

Among the most important physical factors affecting aerosol transport are the size and shape of the constituent particles. The size range of such particles is large; values ranging from 6.7×10^{-4} to 6.7×10^{-3} yds (6×10^{-4} to 10^{-3} m) for urban and natural aerosols have been cited (Corn 1976). In addition to size, the shapes of such particles are highly variable, but may be categorized as spherical, irregular, cubical, flake, fibrous, and condensation forms. The shape of such a particle in an atmospheric aerosol will be a function of the temperature, pressure, fuel, and other factors associated with the local emission source from which it was derived (Corn 1976). Other attendant physical characteristics defining transport capability for such aerosols are density and surface area. In the context of particle size as it affects the properties of atmospheric aerosols, the following factors have been cited: the resistance of the medium, the rate of evaporation, the rate of cooling, the predominance of diffusion or settling, and vapor pressure (Fuchs 1964).

Until the last few years, only a few data were available on many aspects of airborne particles, especially polycyclics and their relative size and weight distribution within aerosols (National Research Council 1972). For example, one study (Demaio and Corn 1966) indicated that 75 percent by weight of a group of polycyclics analyzed were associated with aerosol particles less than 2.5 μm in radius. Another study, however, examining the specific distribution of benzo(a)pyrene per unit weight of soot aerosol found the distribution of the pollutants to be constant (Thomas et al. 1968). In general, few studies have been performed on the mechanics of adsorption of polycyclic organics onto particle surfaces (National Research Council 1972) and, as mentioned in the End Use section of this report, considerable research is needed in this area, especially with respect to adsorption onto particles emitted from coal combustion. The recent state of knowledge, especially with regard to airborne particles, has been summarized by the National Research Council (1979).

In addition to heavier pollutants that are adsorbed onto pollutant or non-pollutant particles, there are organic pollutants that are initially vapors and which subsequently condense. The presence of solid particles in the atmosphere (whatever their nature) promotes the condensation of vapor onto them, and consequently affects their transport capabilities. Particles with a radius smaller than 0.1 μm are referred to as condensation nuclei (Corn 1976). The general term, Aitken nuclei, is often used to refer to such microscopic particles that are the foci of vapor condensation. These nuclei are generated from many sources, especially combustion processes, and they are often pollutants since they may be formed from reactions between various hydrocarbons and nitrogen oxides (Corn 1976).

In addition to the physical and chemical characteristics of the pollutants, extraneous terrestrial and meteorological factors also modify airborne transport. A major terrestrial factor is the topography of the terrain over which pollutants are transported. Terrain that is not flat, or that has various large scale natural or artificial structures on it, may modify the transport of airborne pollutants. Burr and Clymer (1976) have enumerated some of the following meteorological effects that rough, complex terrains may have on the dispersion of airborne pollutants:

- o Channeling of wind by valleys;
- o Boundary layer instability effects;
- o Increased turbulence aloft due to surface roughness;
- o Downflow of colder air into a valley;

Literature Cited

- o Irregular distribution of updraft due to insolation of rough terrain;
- o Turbulence due to wind shear;
- o Nonuniform wind speed and direction due to flow over rough terrain; and
- o Elevation of a "cloud" of pollution caused by inflow of cooler, cleaner air below.

The above list is not meant to serve as a definitive array of factors affecting airborne transport over rough terrain, but it indicates some of the attendant difficulties in predicting the transport and location of such pollutants.

In addition to factors affecting transport, there are transformations that emitted pollutants undergo, either among themselves or with other atmospheric constituents. Such constituents may be particulate, vaporous, or gaseous in nature and may or may not, by themselves, be pollutants. Complex chemical transformations among mixtures of these various components may produce pollutants differing in both nature and amount from the kind originally emitted to the atmosphere.

Perhaps the key or at least a major factor initiating, controlling, and terminating atmospheric pollutant reactions, especially with regard to hydrocarbons, is light energy. From this perspective, the broadest view may be taken on how various vapor or particulate organic pollutants, may interact with themselves and other atmospheric constituents.

For chemical reactions to occur in the atmosphere, it is necessary to have energy input. Atmospheric temperatures generally are not sufficient for this purpose. Light, however, may provide the necessary energy even to initiate reactions subsequently completed in the dark (Haagen-Smit and Wayne 1976). When atmospheric molecules, petroleum-derived organic pollutants, or natural constituents become dissociated due to light energy, they form highly reactive chemical species termed free atoms or radicals. These highly reactive, electrically imbalanced species are of major importance in atmospheric transformations (Haagen-Smit and Wayne 1976). Both organic pollutants and inorganic atmospheric constituents may, under the influence of absorbed light, be converted into these active chemical species. These chemical species then, in a myriad of intermediate reactions, may be transformed into different compounds; or in a series of reactions, they may produce other highly reactive free radicals as products. These in turn may, in a chain reaction, continue the process

(Haagen-Smit and Wayne 1976). Among the classes of organics which can undergo such photodissociation are: aldehydes; ketones; alkyl-, acyl-, and peroxyacyl nitrates; and organic peroxides (Haagen Smit and Wayne 1976). Such large classes of organics all contain pollutants associated with oil or gas production.

It is important to note that this photooxidation of organic pollutants is not confined to compounds that may exist only as a vapor. Photooxidation of adsorbed aromatic hydrocarbons also may occur. It is postulated that the chemical reactivity of hydrocarbons adsorbed on particles is greater than that of hydrocarbons in solution (National Research Council 1972). In experimental studies, such organics as anthracene, naphthacene, benz(a)anthracene, and benzo(a)pyrene have been oxidized under the influence of room or ultraviolet light while in an adsorbed condition (National Research Council 1972).

Rather than attempt to assemble a list of specific organic pollutants and the myriad number of actual or potential products that are, or might be formed from them, this section attempts to delineate some of the more important aspects of atmospheric pollutant chemistry. As a concluding note, some effort has been made to rank organics in terms of their reactivity in relation to their rate of consumption due to photooxidation. This "reactivity" ranking places internally double-bonded olefins as highly reactive; polyalkyl benzenes and monoalkyl ethylenes as moderately reactive; ethylene, monoalkyl benzenes and alkanes as of low reactivity; and benzene, acetylene, methane, ethane, and propane of negligible reactivity (Haagen-Smit and Wayne 1976).

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