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Effects of Atmospheric Deposition of Energy-Related Pollutants on Water Quality: A Review and Assessment

M. J. Davis

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Energy and Environmental Systems Division

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EFFECTS OF ATMOSPHERIC DEPOSITION OF
ENERGY-RELATED POLLUTANTS ON WATER
QUALITY: A REVIEW AND ASSESSMENT

by

Michael J. Davis

Energy and Environmental Systems Division
Integrated Assessments and Policy Evaluation Group

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EXECUTIVE SUMMARY

A number of energy-sector activities release pollutants to the atmosphere. These atmospheric emissions, primarily from combustion, encompass a wide variety of substances -- trace elements, organic compounds, radionuclides, and oxides of sulfur and nitrogen, which may form sulfuric and nitric acid in the atmosphere. Pollutants released to the atmosphere can eventually reach the aquatic environment, where, in original or altered form, they may produce adverse effects. The pathway through the atmosphere to the aquatic environment can be significant for some pollutants; furthermore, its relative significance would increase if direct discharges to bodies of water were reduced or eliminated.

Water-quality effects caused by atmospheric deposition of pollutants are an important environmental issue. Current environmental regulations do not always adequately acknowledge that pollutants are transported from one medium to another. Control strategies aimed at reducing environmental degradation cannot be optimized unless such multimedia effects are considered. This report reviews the effects on surface-water quality that may be caused by atmospheric deposition of pollutants released from energy-related activities. It also makes a preliminary assessment of the adverse effects that may arise from such deposition.

Atmospheric inputs may provide a significant or even a major fraction of certain chemicals delivered to bodies of water. Because atmospheric pollutants deposited on the terrestrial portion of a watershed also influence the aquatic environment, the terrestrial and aquatic environments are coupled and cannot be considered in isolation if aquatic effects are to be understood. Pollutants deposited on land may be transported to bodies of water by either surface or subsurface flows. For example, streams may transport pollutants to lakes, where the pollutants can accumulate in the water column or in sediments. Pollutants actually reaching a water body may be attenuated in quantity or altered in form, compared to atmospheric inputs to the catchment. In addition, different chemicals (e.g., trace elements, acids, nutrients, organic compounds) may be delivered simultaneously and could have synergistic or antagonistic effects.

This report is organized by general category of pollutant -- trace elements, organics, etc. Such an organization helps to point out the sources and effects associated with the various categories of pollutants. However, it focuses minimum attention on the fact that, in general, all types of pollutants will be delivered to the aquatic environment together. This simultaneous delivery occurs because some pollutants are transported over long distances, allowing emissions from different sources to be combined, and also because fossil-fuel combustion produces emissions containing pollutants in most, if not all, groups considered. Pollutants in a complex mixture are likely to interact in terms of effects they produce on biota. The potential effects of individual chemicals on aquatic biota and human health are often not clearly known; the possible synergistic and antagonistic effects from combinations of pollutants are even more poorly understood. Primarily

because knowledge of pollutant interactions is lacking, this report generally treats each category of pollutant in isolation from the others.

A variety of pollutants may reach the aquatic environment from the atmosphere. In this report, categories of pollutants are examined in what is essentially an arbitrary order -- trace elements, acid precipitation, radio-nuclides, organic compounds, and gases.

Aquatic Effects of Atmospheric Deposition of Trace Elements

On a global basis, the quantity of many trace elements released to the atmosphere from anthropogenic sources can be far larger than that from natural sources. Fossil-fuel-related fluxes may exceed natural fluxes by an order of magnitude or more for certain elements. As a consequence, trace-element contamination of the environment is possible. Fossil-fuel combustion is largely concentrated in the middle latitudes of the northern hemisphere. Many trace elements released to the atmosphere are deposited relatively nearby (i.e., within thousands of kilometers). Therefore, one should expect a relatively large potential for adverse effects in the northern hemisphere, particularly in an industrialized region such as the eastern United States, where large amounts of fossil fuels are consumed.

Combustion is the largest energy-related source of trace-element emissions to the atmosphere. The quantity of a particular trace element released to the atmosphere from a specific facility depends on a number of factors, including the type of fuel used, the fuel source, the nature of the plant, and the type of pollution-control equipment used. For most trace elements, coal is the primary fossil-fuel source. The trace-element composition of coal varies a great deal from mine to mine, and even from seam to seam within a mine. Therefore, trace-element emissions will vary a great deal depending on the coal used. The degree to which emissions of fine particulate matter are controlled will also influence the release of certain trace elements to the atmosphere. Releases of trace elements to the atmosphere are not subject to regulation.

The potential terrestrial effects of trace-element deposition appear to be small; observable changes occur only close to the emission source. Regional trends toward increased background concentrations of trace elements are anticipated due to atmospheric deposition over wide areas. However, such increases will usually not be detectable.

Various theoretical and experimental studies have assessed the effects of trace-element deposition on water quality. These studies indicate that deposition of trace elements may cause adverse water-quality effects. In experimental studies, however, it is difficult to separate effects caused by energy-related sources from effects caused by other sources. The theoretical studies to date suggest limited potential for water-quality problems. In this study, several simplified but explicit models for lakes and streams are applied to assess the potential for adverse effects on water quality from trace-element deposition resulting from energy-sector activities. The severity of possible effects is judged by the most recent water-quality criteria.

For streams, adverse effects of trace-element deposition will tend to occur during runoff, when pollutants are flushed from the land surface. Some potential exists for adverse effects on aquatic biota from mercury, possibly from cadmium and, less likely, from chromium. The potential is highest in arid areas. The facts that runoff events are often of short duration and that some matter in runoff is not biologically available should help minimize adverse effects. (The models used in the analysis are not well suited to assessment of the effects of mercury. Therefore, the results for that element are somewhat speculative.)

For lakes, adverse effects result primarily from the accumulation of atmospheric trace elements. Adverse effects would occur primarily in arid areas and in shallow lakes; in such cases, worst-case conditions could result in significant concentration increases for many elements. Primary concern would be for mercury and cadmium. (The models used to assess effects assume no loss of material to sediments. Sedimentation would decrease the magnitude of estimated impacts.)

The probability of dramatic impacts on the aquatic environment due to atmospheric inputs of trace elements released from modern coal-fired power plants seems low. However, the potential for more-subtle, long-term effects in certain areas should not be ignored.

Aquatic Effects of Acid Precipitation

Rain has a particularly low pH in the northeastern United States, in eastern Canada, and in portions of Scandinavia. The low pH is due principally to sulfuric and nitric acids, which various workers have suggested result largely from oxides of sulfur (SO_x) and nitrogen (NO_x) that are released when fossil fuels are burned for power generation and other uses. Energy-related sources of acid precursors are considered significant contributors to the acidity in low-pH rainfall, although the degree of contribution is unquantified. This report assumes that such sources can contribute atmospheric inputs of acids to watersheds and it focuses on aquatic effects.

In this discussion, the term "acid precipitation" includes both wet and dry deposition of hydrogen ions (H^+) and associated anions (sulfate and nitrate). Wet deposition includes those processes in which substances are scavenged by precipitation and carried to the surface in precipitation. Dry deposition includes gravitational settling of particles, aerosol impaction, and sorption of gases at the surface. Both wet and dry deposition may be important; both can produce similar aquatic effects.

In most cases, only a relatively small fraction of acid precipitation is deposited directly on a water body. When precipitation falls on land, the fraction that reaches a body of water unchanged by contact with soil is usually small. A substantial fraction of H^+ may not reach the water. The H^+ ions that are deposited or produced by other constituents in the precipitation may be buffered by reactions in the soil. If calcium or magnesium carbonates are present, H^+ will be consumed and bicarbonate and calcium or magnesium will be released. When no free bases are present, H^+ may be exchanged for metal cations. Some H^+ may react with silicate or other minerals in the soil, releasing metal cations. Hydrogen ions that remain after ion

exchange and mineral weathering will reach the aquatic environment along with leached metal cations and mobile anions, usually sulfate. Electrochemical neutrality requires that, when ions are transported, equivalent amounts of cations and anions move together. Therefore, the transport of H^+ and metal cations from the soil to the aquatic environment requires the presence of mobile anions. Acid precipitation provides sulfate and nitrate as major anions. Nitrate tends to be retained in the soil-plant system of the catchment. Sulfate ions, on the other hand, are often quite mobile.

Large concentrations of H^+ in an aquatic system can affect biota severely. In addition, since the chemical form of many toxic heavy metals depends on pH, and since solubility is a function of species, the mobilization of toxic metals from sediments depends on the concentration of H^+ . In addition to the potential effects of H^+ ions reaching the aquatic environment after their deposition on land, acid inputs to the catchment may cause nutrient leaching from soils and the mobilization of aluminum. Removal of nutrients may reduce soil productivity; mobilization of aluminum may have toxic effects on aquatic biota. Inputs of H^+ to a body of water are episodic. Inputs in snow are delivered to the aquatic environment during snowmelt. The initial meltwater is the most contaminated because pollutants are contained in the intercrystalline brines, which are the first to be washed out. Contaminants in the first meltwater may have concentrations five or more times their concentrations in bulk snow. During the early phases of snowmelt or during a heavy rainfall with low pH, poorly buffered surface waters can undergo a rapid decrease in pH and remain acidic for a short period. Such events associated with snowmelt may produce short-term changes in water quality that are lethal to fish. Mobilization of toxic forms of aluminum also influences the stress on fish at such times. Much of the total annual export of H^+ from a watershed may occur during a short period of spring snowmelt.

Acid precipitation may have significant adverse effects on aquatic biota. These effects may be due to depressed pH or to enhanced concentrations of aluminum or other metals. Fish populations have been reduced or eliminated in significant areas of eastern North America and Scandinavia by acid inputs.

If aquatic resources are to be protected from adverse effects of acid precipitation, then we must know what inputs produce what effects in different aquatic systems. The levels of inputs that an area can tolerate without experiencing additional negative effects must be estimated and the location of the most sensitive aquatic resources must be known. Any rational strategies for controlling pollutant inputs will use such information. Control strategies must also consider the relative importance of nitrate and sulfate in influencing the aquatic environment.

Aquatic Effects of Atmospheric Deposition of Radionuclides

Radioactive substances are emitted to the atmosphere from various stages of the nuclear fuel cycle and also from coal-fired power plants. Environmental effects, including aquatic effects of the light water reactor (LWR) fuel cycle, have received a great deal of attention. Typically, however, the aquatic effects are related to releases of liquid effluents from the fuel cycle. The concern about radiological effects is primarily for

man; effects on other organisms have been less well examined. Atmospheric transport of radionuclides to the aquatic environment usually is not addressed quantitatively in radiological assessments of the LWR fuel cycle. Other pathways of exposure are usually considered significantly more important and the atmospheric pathway to water is neglected.

Aquatic effects (on man and biota) of atmospheric releases from the total LWR fuel cycle should not be of great concern. The major atmospheric emissions are from the reactor and reprocessing stages. Aquatic effects of atmospheric emissions from reprocessing have been quantified; aquatic effects of atmospheric releases from all other stages of the fuel cycle still require quantification.

In addition to trace elements, coal also contains trace amounts of naturally occurring radionuclides. As with trace elements, releases of radionuclides from coal-fired plants are not regulated. Combustion of coal or its conversion to liquid or gaseous forms concentrates the noncombustible trace constituents, including radionuclides, in the ash or releases them in gaseous form. The more volatile radionuclides are also significantly enriched because they associate with small fly-ash particles, which are less efficiently removed by electrostatic precipitators.

A few coal deposits have high concentrations of some radionuclides. These usually are low-grade deposits in the western United States, and make up a possible 0.1% of U.S. western coal reserves. However, in spite of a limited number of deposits with high concentrations of radionuclides, western coals on the average contain smaller quantities of radionuclides (and all trace elements) than other coals.

The effect on human of radionuclides reaching the aquatic environment via atmospheric emissions from coal-fired power plants is probably negligible. The more-direct pathways of ingestion, inhalation, and direct radiation are of little significance, so the much smaller exposure from the pathway involving atmospheric inputs to bodies of water should be of even less concern. None of the studies reviewed in this report examined or even mentioned this pathway, or considered the radiological impacts on aquatic biota.

Aquatic Effects of Other Contaminants Arriving from the Atmosphere

Processes in the energy sector produce a wide variety of organic compounds that subsequently may be released to the atmosphere. A portion of these organics reach the aquatic environment. However, detailed analysis of most organic emissions and assessment of their aquatic effects are not available.

A group of organic compounds that are of some concern are polycyclic aromatic hydrocarbons (PAH). Atmospheric inputs are an important source of PAH to the aquatic environment. The PAH released to the atmosphere are predominantly from inefficient sources of combustion that do not belong to the energy sector. However, coal-refuse burning is one exception that may make a sizable contribution to atmospheric inputs. If home coal and wood burning are considered energy-related sources, they constitute important inputs from

the energy sector. No quantitative assessment of the aquatic impacts of PAH from the energy sector is available.

Combustion of fossil fuels in the energy sector can increase inputs of nitrogen to lakes. However, such increases should not significantly affect water quality unless they are accompanied by increased inputs of phosphorus from other sources. On the other hand, because NO_x and SO_2 are toxic to blue-green algae, direct aquatic effects of energy-sector air pollutants are possible.

EFFECTS OF ATMOSPHERIC DEPOSITION OF ENERGY-RELATED POLLUTANTS ON WATER QUALITY: A REVIEW AND ASSESSMENT

by

Michael J. Davis

ABSTRACT

This report reviews and assesses the effects on surface-water quality of atmospheric pollutants that are generated during energy production. Atmospheric inputs from such sources to the aquatic environment may include trace elements, organic compounds, radionuclides, and acids. These inputs may be delivered together and could produce synergistic or antagonistic effects. Because of a general lack of understanding of such effects, this report focuses on the individual categories of pollutants, usually without considering their effects together.

Combustion is the largest energy-related source of trace-element emissions to the atmosphere. This report reviews the nature of these emissions from coal-fired power plants and discusses their terrestrial and aquatic effects following deposition. Several simple models for lakes and streams are developed and are applied to assess the potential for adverse effects on surface-water quality of trace-element emissions from coal combustion. The probability of acute impacts on the aquatic environment appears to be low; however, more subtle, chronic effects are possible.

The character of acid precipitation is reviewed, with emphasis on aquatic effects, and the nature of existing or potential effects on water quality, aquatic biota, and water supply is considered. The response of the aquatic environment to acid precipitation depends on the type of soils and bedrock in a watershed and the chemical characteristics of the water bodies in question. Methods for identifying regions sensitive to acid inputs are reviewed. The observed impact of acid precipitation ranges from no effects to elimination of fish populations.

Coal-fired power plants and various stages of the nuclear fuel cycle release radionuclides to the atmosphere. Radioactive releases to the atmosphere from these sources and the possible aquatic effects of such releases are examined. For the nuclear fuel cycle, the major releases are from reactors and reprocessing. Although aquatic effects of atmospheric releases have not been fully quantified, there seems little reason for concern for man or aquatic biota. The radiological effects of coal-fired plants are probably insignificant.

A short discussion is presented on organic compounds released to the atmosphere from energy production. Detailed

inventories of such emissions are not available, so thorough assessment of aquatic effects cannot yet be made.

Other aquatic effects of atmospheric releases are possible and are discussed briefly. Combustion produces oxides of nitrogen, which may affect water quality since nitrate is an important nutrient, although usually not a limiting one in most lakes. Nitrogen oxides and sulfur dioxide are toxic to blue-green algae; therefore, direct aquatic effects of gaseous releases from combustion may occur.

1 INTRODUCTION

Energy-related activities can release pollutants to the atmosphere. Some of these pollutants, in original or altered forms, eventually reach streams and lakes, where they may modify the chemical composition of the water. This report reviews the effects on surface-water quality of atmospheric pollutants that are generated during energy production. It also provides a preliminary assessment of adverse impacts that may arise from such inputs.

Energy production can be a source of trace-element inputs to the atmosphere, as well as a source of organics, radionuclides, and oxides of sulfur and nitrogen. Sulfur and nitrogen oxides may form sulfuric and nitric acid in the atmosphere. Atmospheric inputs to the aquatic and terrestrial environment therefore may include trace elements, organics, radionuclides, acids, sulfate, and nitrate, the last of which is a limiting nutrient in some bodies of water.

Atmospheric inputs may provide a significant or even a major fraction of certain chemicals delivered to bodies of water, especially for lakes that occupy a significant fraction of their watershed. In all watersheds, the terrestrial and aquatic environments are coupled and cannot be considered in isolation if aquatic effects are to be understood. Atmospheric pollutants deposited on the terrestrial portion of a watershed influence the aquatic environment.

Atmospheric pollutants are transferred to the surface by processes of wet and dry deposition. In wet deposition, atmospheric pollutants are scavenged by precipitation and delivered to the surface in the precipitation. In dry deposition, gravity causes particles to settle, aerosol particles collide with the surface and gases are sorbed by the surface. Wet deposition is episodic; dry deposition is not. Estimates of pollutant inputs from wet deposition are usually more accurate and more available than estimates for dry deposition, but the processes can be of comparable importance as means of transferring pollutants to the surface. Inputs in wet deposition can be expressed in terms of a concentration in the precipitation. The flux of a pollutant in wet deposition is calculated from its concentration and the precipitation rate. For dry deposition, pollutants are removed from the atmosphere at a rate approximately proportional to the pollutant concentration in air near the surface. The proportionality constant (which has

units of velocity) between the pollutant concentration and the flux of pollutant is called the deposition velocity. Deposition velocity is influenced by properties of the pollutant, roughness of the surface, and atmospheric conditions.

Figure 1 provides a simplified picture of atmospheric input of pollutants to a watershed. Pollutants are transported in the atmosphere away from their source and deposited by wet and dry deposition on land and water surfaces. Pollutants deposited on land may be transported to bodies of water by either surface or subsurface flows. For example, streams may transport pollutants to lakes, where the pollutants can accumulate in the water column or in sediments. Pollutants may also be deposited in snow and then released during periods of snowmelt. The composition of precipitation that falls through a canopy of vegetation may be modified. Pollutants actually reaching a body of water may be attenuated in quantity or altered in form, compared to atmospheric inputs to the catchment. In addition, various inputs (e.g., trace elements, acids, nutrients, organic compounds) may be delivered simultaneously and could have synergistic or antagonistic effects.

This report is organized by pollutant category. Following this introduction, Sec. 2 assesses atmospheric trace elements and their sources, deposition rates, and effects on water quality. Section 3 examines the water-quality effects of acid precipitation. It emphasizes aquatic effects and discusses areas sensitive to acid inputs. Section 4 considers radionuclide emissions from the uranium fuel cycle and from coal-fired power plants. Section 5 reviews the various atmospheric sources of organic compounds and their potential aquatic effects. Section 6 discusses nutrients and gases. Finally, Sec. 7 states the major conclusions based on the material presented in the preceding chapters.

Fig. 1 Atmospheric Inputs of Pollutants in an Idealized Watershed

2 EFFECTS OF TRACE ELEMENTS

2.1 BACKGROUND

Certain elements occurring in trace amounts in the earth's crust are essential for plant and animal metabolism. These essential trace elements, however, can be toxic in excess amounts. Other, nonessential trace elements may also be toxic. The primary natural sources that release trace elements to the atmosphere include windblown dust, volcanoes, and sea spray. Man's activities, especially industrial processes, can mobilize substantial amounts of trace elements and release them to the environment. Important sources of atmospheric emissions include mining, metal production, fossil-fuel combustion, and waste incineration. Energy production may be a significant source of certain trace elements released to the atmosphere.

Energy-related sources that release trace elements to the atmosphere are associated primarily with the coal cycle and oil combustion. Coal-cycle sources include coal-fired power plants, synthetic fuel production, and dust generated in cleaning, storing, and transporting coal. Coal combustion is the major source of trace-element emissions in the coal cycle. Development of synfuel facilities is inadequate to assess their environmental effects, but the atmospheric emissions of trace elements from these facilities should be less than from a power plant that uses a similar amount of coal, since less coal combustion is involved. For example, trace-element emissions from synfuel plants may result from coal combustion for power generation (which may not be on site) or from process steam generation. This section will focus on coal-fired power plants because of their importance as sources of trace-element emissions and because of the probability that their use will increase.

Coal contains all naturally occurring elements, although most are in trace amounts. Its composition varies greatly from source to source and even by location within a given bed of coal. Certain trace elements are commonly enriched in coal as compared to average crustal composition. These elements include antimony (Sb), arsenic (As), boron (B), cadmium (Cd), lead (Pb), mercury (Hg), molybdenum (Mo), and selenium (Se) (U.S. National Committee for Geochemistry, 1980). Since a portion of the trace elements in coal is released to the environment during combustion, these elements may cause environmental impacts.

In combustion, trace elements are released to the atmosphere through a power plant's stacks, which may reach heights of several hundred meters. Discharge at such heights is conducive to the atmospheric transport of trace elements over considerable distances. How far they are transported depends on whether they are associated with small or large particles, or are in the vapor phase. Elements are removed from the atmosphere to the surface of land or water by wet and dry deposition. Trace elements deposited on land may be carried in runoff, either attached to soil particles or in solution, to a body of water. Watersheds retain substantial amounts of these substances, so not all (probably not even most) reaches a body of water. Once in water, the trace elements may undergo chemical reactions, be taken up by biota, be deposited in sediments, or be transported by flowing water. Increased concentrations of biologically available trace elements in surface waters may have adverse effects on the aquatic environment.

The sections that follow review global emission rates of selected trace elements, including those from the energy sector. Emission characteristics of typical coal-fired plants are presented, followed by reviews of the measured impacts of those emissions on soil and water. Then the possible water-quality effects of trace-element deposition are examined.

2.2 TRACE-ELEMENT EMISSIONS TO THE ATMOSPHERE

2.2.1 Overview

As already indicated, there are numerous sources of trace-element emissions to the atmosphere. Table 1 presents estimates of global emissions for a number of trace elements. A detailed breakdown by source sector is not provided, and the numbers given are only approximate. However, the table indicates that, for many trace elements, anthropogenic sources far exceed natural sources.

The numbers in the first four columns of Table 1 are taken from Lantzy and Mackenzie (1979). Principal natural sources of the elements listed are windblown dust and volcanogenic particles. Forest fires, vegetation, and sea-salt sprays may also provide significant inputs. Nriagu (1979) has provided a more detailed accounting for Cd, copper (Cu), Pb, nickel (Ni), and zinc (Zn). His estimates of emissions from natural sources have the same order of magnitude as those shown. The anthropogenic sources in Table 1 are industrial particulates and fossil fuels. Estimates for industrial particulates are likely to be only approximate due to the diversity of industrial sources and the lack of detailed characterizations. Lantzy and Mackenzie (1979) indicate that much of the material emitted by industry may leave the atmosphere near its sources, due to the heights at which emissions are released.

The emission estimates for fossil fuel are based on quantities of fuel consumed, trace-element concentrations in oil and coal, and assumed release factors for each element. The year for which the estimates in Table 1 were made is not stated, but is probably in the early 1970s. Nriagu's (1979) estimates of emissions from coal and oil combustion are of the same order of magnitude for Cd, Pb, and Ni, but smaller by an order of magnitude for Cu and Zn. His estimates of total anthropogenic fluxes of Cu, Pb, and Zn are substantially smaller than those given in Table 1.

The principal fact to be gleaned from Table 1 is that the fluxes of many elements from anthropogenic sources can be far larger than those from natural sources (see the ratios of source inputs in the table). This comparison would hold true even if the results in Table 1 are substantially inaccurate. Since fossil-fuel-related fluxes may exceed natural fluxes by an order of magnitude or more for certain elements, there is a potential for trace-element contamination of the environment from fossil-fuel production. Note that the results in Table 1 are global. Fossil-fuel combustion is largely concentrated in the middle latitudes of the northern hemisphere. Therefore, one should expect an even larger potential for adverse effects in the northern hemisphere and, in particular, in an industrialized region such as the eastern United States, where large amounts of fossil fuels are consumed.

Table 1 Emissions to the Atmosphere of Trace Elements from Natural and Antropogenic Sources

Trace Element	Inputs from Sources (10^8 g/yr)				Ratios of Source Inputs	
	(1)	(2)	(3)	(4)	$\frac{3 + 4}{1 + 2}$	$\frac{4}{1 + 2}$
	Windblown Dust Flux	Volcanic Flux	Industrial Particulate Emissions	Fossil-Fuel Combustion		
Manganese (Mn)	4,250	1,800	3,000	160	0.52	0.03
Cobalt (Co)	40	30	24	20	0.63	0.29
Chromium (Cr)	500	84	650	290	1.61	0.50
Vanadium (V)	500	150	1,000	1,100	3.23	1.69
Nickel (Ni)	200	83	600	380	3.46	1.34
Tin (Sn)	50	2.4	400	30	8.21	0.57
Copper (Cu)	100	93	2,200	430	13.6	2.23
Cadmium (Cd)	2.5	0.4	40	15	19.0	5.17
Zinc (Zn)	250	108	7,000	1,400	23.5	3.91
Arsenic (As)	25	3	620	160	27.9	5.71
Selenium (Se)	3	1	50	90	35.0	22.5
Antimony (Sb)	9.5	0.3	200	180	38.8	18.4
Molybdenum (Mo)	10	1.4	100	410	44.7	36.0
Silver (Ag)	0.5	0.1	40	10	83.3	16.7
Mercury (Hg)	0.3	0.1	50	60	275	150
Lead (Pb)	50	8.7	16,000	4,300	346	73.3

Source: Lantzy and Mackenzie (1979).

2.2.2 Atmospheric Emissions from Energy-Related Activities

Combustion is the largest energy-related source of trace-element emissions to the atmosphere. The quantity of a particular trace element released to the atmosphere from a specific facility depends on a number of factors, including the fuel used, the source of the fuel, the nature of the plant, and the type of pollution-control equipment used. For most trace elements, coal is the primary fossil-fuel source. As already noted, the trace-element composition of coal varies a great deal from mine to mine, and even from seam to seam within a mine. Therefore, trace-element emissions will vary a great deal depending on the coal used. The degree to which emissions of fine particulates are controlled will also influence the release of certain trace elements to the atmosphere.

Table 2 lists emission rates from coal-fired power plants for some trace elements. The Allen steam plant in Memphis, the first entry in the

Table 2 Trace-Element Emissions to the Atmosphere from Coal-Fired Power Plants (kg/1000 MWh)

Element	Allen Steam Plant ^a Memphis, Tenn.	Hypothetical Plant ^b	Hypothetical Plants ^c	
			Cyclone Burners	Pulverized-Coal Burners
As	0.04	0.1	0.005 - 0.06	0.006 - 0.08
Ba	0.06	0.02	0.04 - 0.2	0.08 - 0.4
Cd	0.004	0.01	<0.004 - 0.02	0.005 - 0.03
Co	0.004	0.01	0.006 - 0.02	0.01 - 0.04
Cr	0.06	0.006	0.009 - 0.04	0.03 - 0.1
Cu	0.01	1.0	--	--
Hg	0.02	0.02	0.01 - 0.05	0.01 - 0.05
Mn	0.04	1.0	0.006 - 0.05	0.02 - 0.1
Mo	--	0.2	--	--
Ni	0.02	0.4	--	--
Pb	0.04	0.2	0.007 - 0.4	0.008 - 0.4
Se	0.09	0.02	0.04 - 0.1	0.04 - 0.1
V	0.09	0.2	0.01 - 0.04	0.03 - 0.1
Zn	0.4	1.0	0.05 - 0.8	0.06 - 0.8

^aSources: Klein et al. (1975) and Lyon (1977). Study was of Unit No. 2 of the three-unit Allen plant. The unit was operated at 280 MWe when measurements were made. The plant has cyclone-fed boilers and an electrostatic precipitator with 99.5% efficiency. Feed coal was from southern Illinois or western Kentucky and had a 3.1% sulfur content when tests were made.

^bSource: Vaughan et al. (1975). Study was of a hypothetical 1400-MWe plant that used low-sulfur western coal and had an electrostatic precipitator with 95% efficiency.

^cSource: Dvorak et al. (1977). Study was of hypothetical 1000-MWe plants located in different regions, burning coal from different sources. Plants had electrostatic precipitators with 99.5% efficiency.

table, was studied carefully to develop a budget for trace elements within a plant that employs the best available technologies for particulate control. The other entries in Table 2 represent hypothetical facilities and demonstrate a range of emission rates possible due to differences in coals. Coals commonly vary by two orders of magnitude in trace-element concentrations. For the elements listed, the Allen plant's emissions are usually near the low end of the range expected from the hypothetical plants. In addition to indicating possible ranges in emission rates, the results for the hypothetical facilities are of value as inputs for the water-quality assessments below.

The behavior of trace elements within a power plant varies, depending on how the elements are partitioned among the various streams within a plant. Differences in partitioning appear to relate to the volatility and state of the elements (Klein et al., 1975). On the basis of their studies of the Allen plant, Klein et al. grouped trace elements into three classes: Class I includes barium (Ba), cobalt (Co), and manganese (Mn); Class II includes As, Cd, Cu, Pb, Sb, Se, and Zn; and Class III includes Hg. Chromium, Ni, and vanadium (V) are intermediate between Classes I and II. Class I elements divide equally between slag and inlet fly ash (i.e., before the precipitator). Class II elements concentrate in inlet fly ash more than in slag, and are further concentrated in outlet fly ash. Class III elements remain in the gas phase.

Some elements that volatilize tend to condense or adsorb on fly-ash particles. Because smaller particles have proportionally larger surface areas, elements will tend to be more concentrated on smaller particles, which are less completely removed by precipitators than are large particles. Other elements, like Hg, exit the stack primarily as a vapor. Klein et al. (1975) report that not less than 60%, and probably about 90%, of Hg entering the Allen plant in coal is discharged as vapor. Lindberg (1980) has found, on the basis of limited data for one plant in Tennessee, that there is an absence of gas-to-particle conversion of Hg following release from a coal-fired plant. Because Hg remains in the atmosphere primarily in vapor form, its chances of long-range transport are significant. Andren et al. (1975a) studied Se behavior in the Allen plant and found that the majority of Se was discharged to slag ponds, but that 93% of Se emitted to the atmosphere is in the vapor phase. The elements Cd, Mn, Pb, and Zn in the aerosol of a power-plant plume become more soluble as the distance from the source increases (Lindberg and Harriss, 1980), and the finest particles ($<0.14 \mu\text{m}$) show the largest changes in relative solubility with distance. Those results suggest surface enrichment of trace elements by condensation near the stack.

In the Allen plant, substantial improvement in precipitator efficiency (from 96.5% to 99.5% removal of total particulates) did not decrease the quantities of Cd, Pb, or Zn discharged to the atmosphere (Lyon, 1977). Class I elements are more effectively removed than Class II elements. Electrostatic precipitators can be made more efficient for removing fly ash and most elements, but are less useful for removing elements that concentrate on fine particles, and have no appreciable effect on those that leave in the vapor phase.

2.3 DEPOSITION AND TERRESTRIAL EFFECTS OF TRACE ELEMENTS FROM ENERGY-RELATED SOURCES

Trace elements released by energy production pose a potential problem for water quality. To produce an actual problem, they must be delivered to a body of water and be available to biota. Therefore, the behavior of elements once they leave an emission source can be as important as the actual emission rate. The pattern of deposition of trace elements around a source is a function of atmospheric conditions, topography, and the height at which emissions are released. Tall stacks tend to result in more widespread distribution; consequently fewer effects are observed near the source. The substantial opportunities available for dilution, it has been hoped, would

result in little or no effect farther away; thus the trend has been toward taller power-plant stacks to minimize local air-pollution problems.

As noted earlier, trace-element emissions from fossil-fuel combustion can be comparable to, or exceed, natural fluxes of these elements to the atmosphere. Considerable quantities of toxic trace elements can be discharged from a power plant's stacks. There is interest, therefore, in attempting to measure the environmental consequences of such releases. Since any deposition on land has potential consequences for water quality, this study will first review some of the observations of the effects of deposition on land.

Table 3 outlines some studies on terrestrial effects of trace-element emissions from power plants. The studies listed cover a range of power-plant locations and sizes. Some of the studies observed effects in soils and vegetation, others did not.

If concentrations of trace elements in fly ash deposited on the surface are similar to concentrations in soil, no effect on the soil concentrations would be observed, although the total quantity of trace elements near the surface would increase. Therefore, increases in soil concentrations would be observed only if substantial enrichment of the trace elements occurred on fly ash with respect to soil concentrations. In addition, soil concentrations of trace elements vary naturally, which tends to mask the effect of any trace-element deposition. Wangen and Williams (1978) assume that a 50% concentration increase is needed to detect deposited trace elements. Their calculations indicate that, for a deposition velocity of 1 cm/s, an enrichment factor of nearly 100 would be needed to give such an increase. If the deposition velocity is 3 cm/s, an enrichment factor of about 30 is required. [These calculations are for the point of maximum deposition at the plant they studied (see Table 3). In addition, deposition velocities of 1-3 cm/s are high, although they have been observed for elements associated with large particles. Therefore, the enrichment factors given are conservative estimates.] The conclusion is that natural variability of soil concentration will tend to preclude detection of changes except for elements greatly enriched in fly ash with respect to soil. The elements most likely to be detected are those in the Class II group of elements mentioned above, or those emitted as vapors.

Calculations of atmospheric inputs of trace elements to soils typically assume that the deposited trace elements are uniformly mixed into the soil over some depth and that, in essence, they are indistinguishable from trace elements already in the soil. Trace elements from power plants, however, will tend to be associated with small particles. In addition, many of the more toxic trace elements such as As, Cd, Pb, and Se will tend to be in layers on the surface of these small particles. Therefore, a portion of the deposited trace elements may more readily dissolve or be transported in the solid phase to the aquatic environment than the same elements already present in soil. Difficulty in detecting soil concentration increases does not equate automatically to lack of potential for aquatic effects. However, it does appear that terrestrial effects of trace element deposition will be small and close to the emission source. Regional trends toward increased background concentrations of trace elements are anticipated due to atmospheric deposition over wide areas.

Table 3 Studies of Effects on Soils and Vegetation of Atmospheric Trace-Element Emissions from Coal-Fired Power Plants

Facility Studied	Size (MWe)	Methodology	Effects on Soil	Effects on Vegetation
Four Corners Power Plant, N.M. In operation since 1962. Has two 76-m and two 91-m stacks. ^a	2150	Seventy soil samples were collected on a radial grid around plant and analyzed for Hg.	Measured soil concentrations of Hg were low. Results did not differ significantly from background within 30 km of plant.	---
T.A. Allen Steam Plant, Memphis, Tenn. In operation since 1959; has three 122-m stacks. ^b	870	Soil samples were collected at 1-mi intervals within 20 mi north and south of plant. Moss samples were collected at 2-mi intervals along same transect. All samples were analyzed for numerous trace elements.	No effects were observed in soil samples.	No effects were observed in moss samples.
484-D plant at DOE Savannah River Plant, S.C. In operation since 1952. No precipitator used until 1975. Has a 38-m stack. ^c	83	Soil samples were collected at 15 locations from 1.8 to 16.7 km away from plant and analyzed for numerous trace elements. Cumulative deposition of trace elements was estimated and compared to soil measurements.	Detectable increases of Sr, As, Sb, and Be were predicted in surface soils within 3 km; measurements were largely consistent with predictions.	---
Consumer's Power Co. Plant on eastern shore of Lake Michigan near Holland, Mich. In operation since 1962. Has a precipitator with about 90% efficiency and has a 122-m stack. ^d	650	Soil samples were collected at 45 sites (locations not given) and samples of vegetation were taken at most sites.	Soil was enriched with Ag, Cd, Co, Cr, Cu, Fe, Hg, Ni, Ti, and Zn. Soil enrichments correlate with wind pattern. Less enrichment of Hg was observed than expected.	Plant materials were enriched in Cd, Fe, Ni, and Zn.
Four Corners Power Plant in northwestern New Mexico. Two 800-MW units in operation since 1970 with 97% efficient precipitators. Three other units in operation since 1963 with particulate collection efficiency of 77% until 1972, when improved to 99.2%. ^e	2175	Soil samples were collected at 8, 12, 16, 24, 40, 70, and 120 km downwind from plant, then analyzed for As, B, F, Hg, Se, Sr, U, and V.	Except possibly for Se, concentrations in local soils were not measurably altered. Concentrations of Se near plant may be slightly increased.	---

^aSource: Crockett and Kinnison (1979).

^bSource: Lyon (1977).

^cSource: Evans, Wiener, and Horton (1980).

^dSource: Klein and Russell (1973).

^eSource: Wangen and Williams (1978).

2.4 AQUATIC EFFECTS FROM ATMOSPHERIC INPUTS OF TRACE ELEMENTS

This section discusses trace-element effects in the aquatic environment. It reviews experimental and theoretical studies of aquatic impacts of trace elements that are released to the atmosphere from coal-fired power plants. The potential for aquatic impacts is then assessed.

2.4.1 Perspective on Trace-Element Inputs

As noted earlier, some trace elements (e.g., Pb and Hg) are non-essential -- they have no known beneficial role. Others (e.g., Cu, Co, and Zn) are essential in trace quantities, but are toxic at increased doses. All trace elements are toxic when supplied in overabundance. Trace elements are generally present in natural waters at low concentrations. However, some can be toxic to aquatic biota even at microgram per liter or lower concentrations. Because of the potential for toxicity to aquatic biota (and also to man) and because of the very low concentrations at which toxicity can occur, inputs of trace elements to the aquatic environment are a concern. This section puts trace-element inputs in some perspective. It is not organized as, nor intended to be, a review of the toxicity of trace elements to aquatic organisms. Rather, it briefly presents some basic concepts related to toxicity and provides a basis for evaluating the potential toxic effects of atmospheric trace-element inputs to the aquatic environment.

The response of aquatic life to trace elements depends on many factors. It is, of course, a function of the actual element involved. It also depends on the form of the element in water. That is, the element may be dissolved or particulate, or it may be organic or inorganic. In addition, other chemicals may influence an organism's response to a trace element by promoting antagonistic or synergistic effects. A number of additional physical, chemical, and biological factors influence the effect of trace elements on aquatic organisms. The following outline is based on the presentation by Prosi (1979).

The following physical and chemical factors influence the toxicity and uptake of elements by aquatic organisms:

- Temperature and dissolved oxygen. Increased temperature results in increased respiratory activity and increased toxicity. The dissolved oxygen concentration also influences metabolism and the absorption and release of trace elements. Temperature and dissolved oxygen can also modify their availability through influences on chemical processes.
- Water hardness. Toxicity is influenced by hardness when the trace element forms soluble carbonate complexes or is adsorbed on calcium carbonate. The concentration of a trace element needed to produce a certain level of effect generally increases with water hardness. The toxicity of some elements, such as mercury, is largely unaffected by water hardness.

- Presence of organic compounds. Organic compounds can decrease the effects of trace elements by forming complexes with them. This complexing may also increase the movement of trace elements by remobilizing them from sediments.
- pH. The pH plays an important role in aquatic chemistry by influencing chemical reactions and the speciation of trace elements.
- Salinity. In estuaries, salinity can play an important part in determining trace-element concentrations.

A number of biological factors also influence the concentrations of trace elements in aquatic organisms:

- General physiologic behavior. Concentrations in freshwater and marine organisms must be considered separately due to differences in osmotic regulation.
- Life cycle and life history of organisms. Effects of trace elements can vary with the age of an organism or its stage of development (e.g., egg, larva). Concentrations in organisms can also be a function of the organism's mobility, since this determines uniformity of exposure to sources of trace elements.
- Seasonal variations. The metabolism and fat content of an organism may change with the season and thus influence trace-element concentration. The activities of organisms and quantity of biomass also vary, influencing trace-element concentrations in water and thus the availability of the elements.
- Species variability. Concentrations in organisms can be influenced by trophic level and by physiologic structure (e.g., how respiration occurs).

As the lists above indicate, a variety of abiotic and biotic factors influence the effects that may result from trace-element contamination of the aquatic environment. These factors must be considered in evaluating such effects. Given the number of possible contaminants, the number of possible species, their interactions, and the various factors involved, the problem becomes quite complex.

To assess the potential for adverse effects of trace elements on aquatic biota, criteria developed by the U.S. Environmental Protection Agency (EPA) will be used. The EPA has recently published water-quality criteria for a number of toxic pollutants, including various trace elements. The availability of the documents describing these criteria is given in the Federal Register (Nov. 28, 1980a). Appendix A summarizes criteria for some trace elements for freshwater aquatic life, human health, and domestic water supply.

The criteria developed by EPA for aquatic life are intended to protect most (but not always all) aquatic life and its uses. The criteria are intended "to protect most species in a balanced, healthy aquatic community" (Federal Register, Nov. 28, 1980b). They generally are not related to

the various factors given above, or expressed in terms of a specific organism or season, or, generally, in terms of chemical or biological factors (criteria for some elements are presented as a function of water hardness). Various factors were, of course, considered in developing the criteria, although some criteria are based on limited information. They do not represent, and were not intended to represent, any absolute natural constants. They do provide a rational, explicit basis for assessing the potential for impacts.

2.4.2 Previous Studies

The toxicity of trace elements to biota and the possibility of trace-element concentrations reaching undesirable levels in water supplies are subjects of concern. One possible route by which trace elements reach the aquatic environment is from the atmosphere. A limited number of studies exist of aquatic impacts due to atmospheric trace-element inputs, especially due to emissions from energy-related sources. Table 4 outlines some studies of atmospheric inputs to the aquatic environment.

The first study cited in Table 4 involves a small lake adjacent to a large coal-fired power plant. The study found no serious effects involving Hg after seven years of plant operation. It does show statistically significant increases of Hg concentrations in sediment compared to concentrations before the plant began operation. Soil concentrations of Hg were also significantly larger downwind of the plant than in other directions.

The second case in the table has numerous sources of trace element inputs for the small research watershed described. These include three coal-fired plants within 20 km. The authors indicate that certain trace elements reaching the watershed may originate from the power plant, including more than about 20% of the load of As, Cr, and Se.

The third study described in the table attempts to measure changes in trace-element concentrations in bulk precipitation at a small pond located 5 km from a coal-fired plant when more efficient particulate controls were installed in the plant. No significant changes in the concentrations in bulk precipitation were observed, implying that the power plant was not a major source of aerially deposited trace elements for the pond.

The other studies in the table involve Lake Michigan. Based on possible emissions sources, energy-related activities should provide a significant part of atmospheric trace-element inputs to the lake. They cannot be separated from other sources, however, in experimental studies that measure atmospheric deposition. The key point made by the Lake Michigan studies is that atmospheric inputs are an important source of trace elements in the lake. The relative importance of atmospheric inputs of any material tends to increase with the portion of a drainage basin's surface area that is occupied by water. Since the ratio of water to land surface in the Lake Michigan basin is high, atmospheric inputs are expected to be significant.

Experimental studies have provided limited help in assessing the potential effect on surface-water quality from atmospheric trace elements that are emitted from power plants. Such studies are difficult to perform due to competing sources and the extensive effort involved. At this stage,

Table 4 Experimental Studies of Atmospheric Trace-Element Inputs to the Aquatic Environment

Location and Data Source	Source of Trace Elements	Methodology	Conclusions
Lake Sangchris, central Illinois (87.2 ha surface area). Source: Anderson and Smith (1977).	The principal source is a 1200-MW coal-fired power plant with 152-m stacks and 98%-efficient electrostatic precipitators, located adjacent to the lake in the central portion of the watershed; the lake extends 6-7 km away from the plant in the direction of prevailing winds.	Seven years after plant began operation, soil, lake sediment, and biota were analyzed for mercury.	Mercury was not implicated as a serious pollutant of the lake or surrounding soil. Concentrations in fish in the lake were unusually low for unknown reasons. Statistically significant increases were observed in soil and sediment concentrations of mercury (see text).
Walker Branch Watershed, Oak Ridge, Tenn. (97.5 ha catchment area). Sources: Andren and Lindberg (1977) and Andren, Lindberg, and Bate (1975).	Numerous possible sources include three coal-fired power plants within 20 km with a total coal consumption of about 7×10^6 ton/yr. Precipitator efficiencies of the plants are 85-90%.	Researchers measured wet and dry deposition, analyzed water samples, and attempted to determine sources of elements by using enrichment factors and a chemical mass-balance approach. They also determined trace-element budgets for the watershed.	Based on enrichment factors, inputs of Zn and possibly Hg can be attributed to power plants. Mass balance indicated that no more than 5% of total aerosol input is from power plants; 20% or more of the load of As, Cr, and Se may be from power plants.
Skiff Pond, South Carolina (2 ha surface area). Source: Wiener (1979).	The pond is located 5.5 km from an 83-MW coal-fired power plant with 38-m stacks. Prior to 1976, fly ash was controlled by cyclone collectors with efficiencies of about 75%. In late 1975 and early 1976, precipitators with efficiencies greater than 99% were installed.	Cadmium, Cu, Mn, and Pb were analyzed in bulk precipitation for 21 months.	No significant changes in the mean concentrations of these elements in precipitation were observed.
Southern Lake Michigan. Source: Dolske and Sievering (1979).	Numerous sources include the industrialized southwest shore.	Researchers measured dry deposition at a midsouthern lake site for five months in 1977.	Dry deposition appears to be an important source of Mn (19%), Zn (30%), and Pb (60%) for the southern basin.
Lake Michigan. Source: Eisenreich (1980).	Numerous	Scientists measured bulk deposition at 21 locations around lake from Sept. 1975 through Dec. 1976.	Atmospheric input provides an important source of Mn (10%), Cd (10%), Cu (13%), Zn (33%), and Pb (60%). Deposition is greater in the southern basin; the deposition pattern implicates the southern boundary of the lake as the primary source of inputs.
Southern lake Michigan. Source: Muhlbaier and Tissue (1981).	Numerous	Researchers developed a budget for Cd based on measured atmospheric and other inputs.	Atmospheric input of Cd was estimated at 60% of total. The input rate of Cd exceeds loss rate by a factor of 2.5. If a modest rate of increase in Cd input is assumed, Cd concentration may increase in several decades to the point where deleterious effects on zooplankton may occur.

mathematical models are more likely to provide a better assessment when a number of pollutants and locations are of interest. Such assessments also pinpoint areas that need further experimental work.

Table 5 outlines several such assessments that have been performed. The first two suggest that water-quality problems are unlikely to result from atmospheric trace elements emitted from coal-fired power plants. The other two studies involve atmospheric inputs to Lake Powell in Utah on the Colorado River. These studies indicate a potential problem from mercury deposition.

Vaughan et al. (1975) assessed the effects of a 1400-MW plant with electrostatic precipitators (95% efficient) and a 300-m stack. The assessment for water-quality effects was for the Southwest, but meteorological data for St. Louis appears to have been used. The study assumed that runoff contained 0.1% of the concentration of trace elements in the soil. Soil concentrations were enhanced by deposition over 40 years of plant operation. Thirty trace elements were considered. The researchers assumed all deposited trace elements were biologically available, while only a fraction of the background soil concentration of each was available. The fraction available varied by trace element.

The study by Vaughan et al. uses a conservative approach: low precipitator efficiency, long plant operation, and biological availability of all inputs. However, emission rates for the hypothetical plant (see Table 2) are not as large as one might expect on the basis of such a low precipitator efficiency. This holds true for many elements considered, but especially for As, Ba, Cr, and Se, as compared with the low end of the emissions range quoted from Dvorak et al. in Table 2. For As, Cr, and Se, Vaughan et al. use concentrations in coal of 5 parts per million (ppm), 0.3 ppm, and 1 ppm, respectively. The corresponding emission rates are 0.1 kg/10³ MWh, 0.006 kg/10³ MWh, and 0.2 kg/10³ MWh (with a 95%-efficient electrostatic precipitator). For a Wyoming coal, Dvorak et al. use concentrations of 1 ppm, 5.8 ppm, and 0.8 ppm for As, Cr, and Se; emissions are 0.05 kg/10³ MWh, 0.009 kg/10³ MWh, and 0.04 kg/10³ MWh (with a 99.5% efficient electrostatic precipitator). The plant has a 300-m stack, which deposits only a small fraction (6%) of the trace elements within 50 km of the plant. Different assumptions could have resulted in larger deposition rates and, consequently, higher concentrations of elements in water. The assumption that the concentration of all trace elements in runoff water is 0.1% of that in soil has little justification; considerable variation would be expected for different areas and different elements. The study did not consider effects due to multiple sources.

Dvorak et al. (1977) used a different approach to assess the effects from a coal-fired plant. Their assessment considers five different plant locations and coal types, resulting in the range in emission rates given in Table 2. The total emissions from a 1000-MW plant are assumed to be diluted by a 28.3 m³/s (1000 ft³/s) flow having an existing concentration typical of each region studied. Relative increases in concentration were calculated, as well as the resulting total concentrations, which were compared with water-quality criteria.

Table 5 Theoretical Studies of Effects on Surface-Water Quality of Atmospheric Emissions from Coal-Fired Power Plants

Location(s) and Data Source	Facility		Stack Height (m)	Methodology Used	Projected Effects
	Size (MWe)	Control Technology			
1. Great Basin (Southwest U.S.). Source: Vaughan et al. (1975).	1400	95%-efficient electrostatic precipitator, low sulfur coal, no scrubbers.	300	- Attempted to determine maximum credible exposure concentration. - Used atmospheric dispersion and wet and dry deposition models. - Assumed that concentration of available trace elements in runoff water equals a fraction (10^{-3}) of estimated concentration in soil after 40 yr of plant operation. - Considered 30 trace elements.	Such a plant does not present major concerns and has no likely adverse effect on drinking water. Largest concentration increases in runoff are for Cu, Hg, and Mo.
2. Five locations considered: - Northern Appalachia - Southern Appalachia - Eastern Interior - Four Corners - Pacific Northwest Source: Dvorak et al. (1977).	1000	99.5%-efficient electrostatic precipitator. Scrubbers also used with high-sulfur coal; coal type depends on region.	300	- Attempted worst-case assessment. - Assumed that total emissions for each element were diluted by a $1000\text{-ft}^3/\text{s}$ flow. - Found percent increase in average background concentration for each location. - Estimated concentration for hypothetical lake at the location of maximum deposition, with 30-yr accumulation of input. - Considered 21 trace elements.	Impacts from a single plant are unlikely for the lake or for a stream with flow of $1000\text{ ft}^3/\text{s}$ or more. Overall potential for problems, in order, is: Cd, Hg > As, Cr, Pb, Se, Zn > Ba, Cu, Mn > Co, Mo, Ni
3. Southwest Utah. Source: Walther (1976).	(a) 3000	99.5% efficient electrostatic precipitator.	183	- Used dispersion and dry deposition model for emissions from the two sources. - Estimated inputs for Lake Powell. - Assumed all deposition in watershed reaches lake within a year. - Input to lake is diluted by yearly flow into lake. Calculated concentration compared with background. - Considered 40 substances.	Mercury is the only pollutant with a potential for a problem, but then only if projected increase in concentration is compared with lowest measured concentration for lake.
	(b) 2000 (estimated)	99% efficient electrostatic precipitator.	236		
4. Southwest Utah. Source: Wagenet, Grenney, and Jurinch (1978).	a	a	a	- Used a dispersion and dry deposition model (assumed 75% of emissions were deposited in impact area) and an erosion and sediment transport model. - Found cumulative load to lake over a 25-yr period. - Model has not been validated. - Considered Zn, Cr, Pb, Cd, and Hg.	After 25 yr, 83% of Hg load and 6% of Cd load are from power plant. Increases of loads of other elements are insignificant. No water quality effects were considered.

^aNot stated but should be similar to 3(a).

The assessment by Dvorak et al. is conservative because all emissions are assumed to reach the water. The $28.3 \text{ m}^3/\text{s}$ flow is based on the capacity needed to site a large power plant. The primary criticism of this approach is of its use of the $28 \text{ m}^3/\text{s}$ flow for determining dilution. The water-quality criteria used for comparison (apparently for drinking water supply) are high for certain elements (e.g., Cd, Cr, Cu, Hg, Pb, Zn) in comparison with more recent EPA ambient-water-quality criteria. Use of smaller dilution flows and more stringent criteria would modify the conclusions reached in the study. The approach would be improved by evaluating dilution effects more carefully, by examining several actual basins, and by including the possibility of multiple power plants.

Dvorak et al. also examined the potential for water-quality effects in a lake located in the area of maximum deposition for the plant considered. They treated the lake as a closed system with a 30-yr accumulation of atmospheric deposition. Their analysis indicated no excessive concentrations for any element in the lake. However, they neglected background concentration and any inputs to the lake from its drainage area. Correcting these omissions, plus considering a larger plant and a more shallow lake, might change the conclusions.

2.4.3 Assessment of Aquatic Effects

Several assessments of water-quality effects of atmospheric trace-element inputs from coal-fired power plants have been reviewed. Two of these provide a general assessment of the potential for adverse effects. For surface freshwater systems, assessments are needed of impacts on streams and lakes. Vaughan et al. (1975) consider only streams (actually runoff). Their assessment is detailed, but assumes a rather arbitrary relation between trace-element concentration in soil and in runoff. Dvorak et al. (1977) examine both streams and lakes. However, their assessment for streams is based on a $28 \text{ m}^3/\text{s}$ stream receiving all emissions. Their lake assessment was based on a body of water with no outflow and no inputs from its watershed.

This section provides another assessment of the potential for impacts on streams and lakes. The approach uses simple, explicit models that illustrate the major parameters involved in the analysis. The models provide a conservative assessment and illustrate regional variability. Impact is evaluated by comparing results with the most recent water-quality criteria from EPA.

Since some portion of the trace elements deposited in the terrestrial portion of a basin eventually reaches the aquatic environment, the first part of this section discusses retention of trace elements in watersheds. Then the models used to assess impacts are presented. Finally, the results of lake and stream assessments are considered.

Trace-Element Accumulation in Watersheds. Only a limited number of studies are available to help answer the following questions: Given atmospheric deposition of trace elements in a watershed, what fraction of trace elements that are deposited is retained by the terrestrial portion of the watershed, and what fraction is exported in a streamflow? How does this

retention depend on the trace elements involved and the character of the watershed, and how does it vary with time? Definitive answers are not available, but it seems reasonable to expect that a substantial fraction of trace-element input is retained by soils and vegetation. This fraction is difficult to quantify accurately.

Relevant studies have been performed in the Walker Branch Watershed in eastern Tennessee and in the Hubbard Brook Experimental Forest in central New Hampshire. Van Hook et al. (1977) measured wet and dry deposition and examined budgets for Cd, Pb, and Zn in the Walker Branch Watershed, which has an area of 97.5 ha and is covered by a mixed deciduous forest. Annual losses of Pb in streamflow were equal to 2% of the atmospheric input, and litter and soils were the major sinks; annual output of Zn was 26% of estimated input; annual loss of cadmium (based on 6 months of data) was estimated at 33% of input. The watershed soil was the major sink for all three elements. Lindberg et al. (1979) obtained estimates of atmospheric inputs (in both wet and dry deposition) for Cd, Pb, Mn, and Zn for Walker Branch for calendar year 1977. Their results were: Cd, 5.2 g/ha; Pb, 150 g/ha; Mn, 350 g/ha; and Zn, 93 g/ha. These appear to be the best available estimates of inputs for this watershed. Turner et al. (1977) estimated trace-element export from the watershed in streamflow for the period from August 1975 through September 1976. For Cd, they estimated an export of 0.15 g/ha; for Pb, 2.2 g/ha; for Mn, 193 g/ha; and for Zn, 12.4 g/ha. These estimates cannot be compared directly to the estimates of inputs by Lindberg et al. (1979) because of the different time periods used. Considerable variability is expected in both inputs and outputs for different years. However, with the exception of the estimates for Mn, the results indicate that the watershed is retaining a substantial portion of the input. Since the fraction exported is small, the relative change in the estimated fraction retained will be small even if estimates of input and output change considerably. Using the results for the two different periods gives estimates of watershed retention as follows: Cd, 97%; Mn, 45%; Pb, 99%; and Zn, 87%. If the Cd export estimate were too small by a factor of two and the input estimate were too large by a factor of two, then the fraction retained would be 88%. In other words, a very large fraction of the Cd, Pb, and Zn is retained. A sizable fraction of the Mn may be exported. However, the study by Turner et al. (1977) concluded that the order of trace-element export was:

$$\text{Cd} < \text{Cr} < \text{Cu} < \text{Pb} < \text{Zn} < \text{Mn} < \text{Fe},$$

which is similar to the probable order of abundance of trace elements in the soils and rocks of the watershed. Therefore, much of the export of the elements may be due to natural weathering.

Siccama and Smith (1978) constructed an input-output budget for Pb for a portion of the Hubbard Brook Forest. Watershed No. 6 was studied for the year 1975. The watershed has an area of 13.23 ha and is a northern hardwood-forest ecosystem. The predominant soil is a sandy loam. They determined Pb input in precipitation and Pb output in streamflow. On the basis of the input and output, the system appeared to retain 97% of the Pb input. In a continuation of the study of Watershed No. 6, Smith and Siccama (1981) studied the Pb budget for a total of four years (1975-1978). They obtained an average annual input of Pb in precipitation of 266 g/ha and a total average annual output in streamflow of 6.1 g/ha, corresponding to a 98% retention of the

input. Of the 6.1 g/ha exported, 1.1 g were associated with particulate matter and 5.0 g were either in solution or in fine particles. Smith and Siccama (1981) suggest that the natural geologic output of the watershed is on the order of 1 g/ha/yr. Elimination of the Pb in precipitation may reduce the output by about 5 g/ha/yr. The authors state that Pb export is most likely significantly related to Pb input from direct precipitation on the stream, whose channel occupies 1.5% of the watershed's area. For the period studied, the amount of Pb deposited in the system decreased by 40 g/ha/yr, probably because use of leaded gasoline decreased. Continued decrease in input may result in lower output, primarily in the dissolved load of the stream.

In the long term, trace elements arriving from the atmosphere may reach a steady state in which outputs approach inputs. Long-term records of atmospheric deposition for Walker Branch are not available, so it is not known if current deposition rates have existed for some time and if an equilibrium has been reached. Continued input at the present rate could result in increased exports in the future. The input rate for Pb at Hubbard Brook appears to be decreasing, on the basis of four years of measurements.

Benninger et al. (1975) have discussed the use of ^{210}Pb as a tracer for studying heavy-metal retention in watersheds. They indicate that a large fraction of ^{210}Pb deposited from the atmosphere is retained in the organic fraction of the soil. They took 1-1/2 yr of data in the northeastern United States on wet and dry deposition of ^{210}Pb and quantities of ^{210}Pb in soils, which are in steady state with respect to these atmospheric inputs. They report that, within the uncertainties of their measurements, the soils retain virtually all atmospheric input. The ^{210}Pb is homogenized within the organic-rich layers of the soil.

The studies of trace-element budgets have not yet answered the questions posed at the beginning of this section. The watersheds studied are retaining large fractions of atmospheric inputs. How this retention varies with trace-element and watershed characteristics was not clearly answered, nor was the question of long-term variability in export. The studies do show that a simple ratio of output to input implies a retention of from about 50% to 99% for various elements. The smaller number (50%) for retention is for Mn and was estimated for Walker Branch using inputs and outputs for different years. While retention of inputs near the upper end of the range (i.e., 99%) was observed in a number of cases, the lower end of the range of retention is not well defined. For a watershed in which atmospheric trace-element inputs are all retained in soils, and in which little weathering occurs, the output approaches the quantity of material deposited directly on the stream channel. Such a case would define a lower limit for export (probably near 1% of inputs). When output is well above this limit, much of the export may be due to natural weathering. This may well be the case for Mn in Walker Branch. From an order-of-magnitude perspective, the results suggest that export of atmospheric inputs (especially when natural weathering is included) does not approach 100% of input. Therefore, for forested areas, one might roughly estimate that export of atmospheric inputs ranges in order of magnitude from 10% to less than 1% of atmospheric inputs. These are only order-of-magnitude estimates based on small samples and for a limited number of trace elements.

For the lake assessments below, 10% of atmospheric input is assumed to be transported annually from land to a body of water. This estimate is

conservative, since it is near the high end of the range of results observed. How this number might vary for types of watersheds other than those studied has not been quantified.

Models Used for Assessment. Three models are used in this study for assessing the potential for impacts on surface-water quality due to atmospheric inputs of trace elements. The models are described in detail in the appendix, where all results presented here are derived.

The stream model assumes that all material deposited from the atmosphere in the course of a year is removed by, and diluted in, annual runoff from the basin. This considerably overestimates the material removed from the land surface. Larger concentrations might occur during certain periods such as snowmelt, when deposited material might be transported over frozen ground in a small amount of runoff. Therefore, the approach does not provide a rigorous upper limit for all events. It is reasonably conservative since it overestimates the mass of contaminant. In addition, in application, a small annual runoff will be used. The approach assesses effects only during wet weather. During dry weather, only inputs directly to the stream channel would produce aquatic impacts. Since a stream has a small surface area compared to an entire basin, dry-weather effects should be small.

Two types of lakes are considered, one with an outlet, one without (a closed basin). For the lake with an outlet, the appendix shows that, in equilibrium, and assuming conservative behavior, the concentration of a trace element in the lake is given by:

$$C = C_{in} + \frac{\phi(1 + \alpha\gamma)}{P(\gamma g + 1) - E} \quad (1)$$

where:

C_{in} = concentration of the trace element before atmospheric deposition begins,

ϕ = deposition rate of trace element (mass/unit area/yr),

α = fraction of atmospheric input delivered from land to the lake,

γ = ratio of land area to lake area in basin,

P = annual precipitation (depth/yr),

g = fraction of precipitation on land surface that reaches the lake, and

E = annual evaporation from the lake (depth/yr).

The denominator in the expression above, which represents annual discharge from the lake, is positive. Equation 1 states that, in equilibrium, the concentration of a trace element in the lake is given by its initial concentration plus an increment that equals the annual mass added to the lake surface or transported to the lake from its watershed, divided by the annual outflow from the lake. The factors in the equation are normalized so that only relative sizes of land and lake are important. Assuming a well-mixed system in equilibrium, the expression applies equally to a large lake or a

small pond. The parameters ϕ , α , γ , P , g , and E can be varied to account for regional differences. The use of an equilibrium condition assumes that no large hydrologic changes occur.

For a closed basin, the expression for concentration of a trace element is:

$$C = \frac{\phi}{d} (1 + \alpha\gamma)t + C_0 + \left\{ \begin{array}{l} \text{trend due to} \\ \text{other inputs} \end{array} \right\} \quad (2)$$

where:

d = mean depth of the lake,

t = time period (yr) for which atmospheric inputs have been applied, and

C_0 = the initial concentration in the lake.

In the idealized closed basin, concentration increases linearly with time. Inputs of trace elements (equivalent to $\alpha\gamma\phi$) from the land surface are included, but no additional dilution due to runoff is provided.

The two lake models are conservative since they assume that all trace elements remain in the water column (i.e., no loss to sediment occurs). Such losses are probably substantial for most trace elements in most lakes.

Assessment of Effects. The assessment procedure is detailed in the appendix. Atmospheric emission and deposition rates are based on the results by Dvorak et al. (1977). Two situations are considered: a power plant at an eastern interior site that burns Illinois coal, and a facility at Four Corners in the Southwest that uses western coal. The plants have a capacity of 1000 MWe, use pulverized-coal burners, operate at 70% of capacity, and have electrostatic precipitators that remove 99.5% of total particulates. The two locations and coals provide regional differences in coal composition and meteorology. The two coals largely encompass the emissions range of the various coals considered by Dvorak et al.

A variety of deposition rates were calculated for each trace element considered. The calculations assume that all trace elements are associated with particulates. This is probably a valid assumption, except for Hg. Mercury remains in the atmosphere primarily in the vapor phase following release from coal-fired plants (Lindberg, 1980). Table A.2 shows that dry deposition rates for all trace elements (except Zn at the eastern site) are $10 \mu\text{g}/\text{m}^2/\text{yr}$ or less. Including wet deposition would increase the annual deposition rate. Measured deposition rates for a variety of trace elements show that substantially larger deposition rates commonly occur in many locations (not necessarily related to coal combustion). Rates are often in the $\text{mg}/\text{m}^2/\text{yr}$ range (Lindberg et al., 1979; Eisenreich, 1980). The Committee on Lead in the Human Environment (1980) reports lead deposition rates of $6\text{--}34 \text{ mg}/\text{m}^2/\text{yr}$ for rural locations. Table A.2 shows values typically less than $10 \mu\text{g}/\text{m}^2/\text{yr}$ and less than $0.3 \text{ mg}/\text{m}^2/\text{yr}$, even assuming all deposition is within 50 km of the plant. Therefore, the deposition of emissions from a single coal-fired plant of the type considered are small compared to what is commonly observed in many locations.

For a stream, the annual deposition rate divided by annual runoff gives a conservative estimate of the increase in trace-element concentration. This assessment uses an annual runoff of 2 cm, which is very small. (Equal or smaller values are found only in arid portions of the West. Runoff of 25-75 cm is the norm east of the Mississippi River.) Table A.2 shows annual deposition rates from a single 1000-MWe plant to be $10 \mu\text{g}/\text{m}^2$ or less for all elements except Zn. Adding wet deposition would increase these values; the amount of increase depends on the ratio of wet to dry deposition. Dry deposition will tend to dominate in arid areas and wet deposition will tend to dominate in wet areas. If wet deposition dominates, then the absolute amount of dry deposition will tend to decrease compared to the estimates given in Table A.2, since total emissions to the atmosphere remain constant. In arid areas with dry deposition dominating, the $10 \mu\text{g}/\text{m}^2/\text{yr}$ estimate for deposition is reasonable, as is the 2 cm runoff. For areas with high rainfall and with a runoff of 25 cm or more, wet deposition may dominate but a ten-fold increase in the total deposition would be required to produce the same ratio of deposition to runoff as found in the West. Since emissions of trace elements are independent of deposition, there is a limit to the increase in total deposition possible. In light of the difficulty of estimating total deposition, the analysis here considers only dry deposition, while acknowledging qualitatively the possibility of enhanced effects due to wet deposition. For an arid location, which provides conditions close to worst-case, the input of $10 \mu\text{g}/\text{m}^2/\text{yr}$ diluted in a runoff of 2 cm/yr yields a concentration of $0.5 \mu\text{g}/\text{L}$.

The appendix presents water-quality criteria for water supply and protection of human health. A concentration of $0.5 \mu\text{g}/\text{L}$ is more than an order of magnitude less than the criteria for all elements listed except Hg, which has values of $2 \mu\text{g}/\text{L}$ for water supply and $0.144 \mu\text{g}/\text{L}$ for protection of human health from ingestion of Hg through water and contaminated aquatic organisms. The smallest value for the other elements is $10 \mu\text{g}/\text{L}$. The quantity of a trace element diluted in runoff may well be 10% or 1% of the annual deposition rate. If only one-tenth of the material deposited is removed, then the estimated concentration ($0.05 \mu\text{g}/\text{L}$) is two orders of magnitude less than all drinking-water and human-health criteria except those for Hg, for which it is one order of magnitude and about three times less, respectively. Therefore, even with a sizable increment of wet deposition and the uncertainty of dry-deposition estimates, inputs of trace elements from a single power plant should not produce concern for human health. Inputs of mercury are the sole possible exception; however, the approach used here has a limited ability to assess effects due to Hg input, since the element exists primarily in the vapor phase -- this analysis assumes trace elements are associated with particles in the atmosphere.

Comparing trace-element inputs with the criteria for freshwater aquatic life is more complicated. The criteria for Cd, Cr, Pb, and Zn depend on water hardness (see appendix). A hardness of 100 mg/L as CaCO_3 (moderately hard) is reasonable* for arid conditions. Criteria are specified two ways: a 24-h average, and an upper limit that may not be exceeded at any time. For the latter, all of the trace elements considered have an upper limit of about

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*Reasonable in the sense that hardness is probably underestimated, yielding criteria that are underestimated (if they depend on hardness) and therefore conservative.

two or more orders of magnitude greater than the estimated concentration of 0.05 $\mu\text{g/L}$, except again for Hg, for which the criterion is 0.0017 $\mu\text{g/L}$. For a 24-h average, only Cd (0.025 $\mu\text{g/L}$), Cr^{+6} (0.29 $\mu\text{g/L}$), and Hg (0.00057 $\mu\text{g/L}$) do not have criteria that are orders of magnitude above 0.05 $\mu\text{g/L}$. The 24-h criteria would be appropriate only if high-flow periods that remove trace elements persist as long as 24 h.

The freshwater-life criteria are for "total recoverable" concentrations, not total concentrations. "Total recoverable" refers to all dissolved forms (defined operationally as material passing through a certain size filter), plus material brought into solution in an analytically determinable form by a specific pretreatment of the sample. This includes material sorbed to particulate matter. Material present in particulate matter may or may not be brought into solution by pretreatment. The criteria, therefore, refer to only a fraction of each chemical being transported.

The conclusion of the stream assessment is that some potential exists for adverse effects on aquatic biota from mercury, possibly from cadmium, and less likely from chromium. The potential is highest in arid areas. The facts that runoff events are often of short duration and that some matter in the runoff is not biologically available should help minimize adverse effects. The conclusions are sensitive to the duration of the runoff and are based on a single, modern, 1000-MWe plant. Again, the limited availability of the analysis to properly deal with Hg must be noted.

Retention of trace elements in stream sediments was not considered. Conceivably, trace elements could be retained in sediments and then re-suspended after considerable accumulation has occurred. Background concentrations of trace elements would increase the total stream concentration. However, the estimated increase in concentration must still be a significant fraction of the relevant criteria before any concern about atmospheric inputs would be warranted.

The next model considers a lake with an outflow and atmospheric inputs to its surface and the land portion of its basin. If the deposition rate is 10 $\mu\text{g/m}^2/\text{yr}$ and 10% of atmospheric deposition is exported from the land surface, trace-element concentrations will increase as shown in Table 6. Results are presented for a variety of locations in the conterminous United States that exhibit a wide range in precipitation and runoff.

The analysis uses a model with six parameters: deposition rate, annual precipitation and evaporation, annual runoff coefficient, fraction of atmospheric deposition exported (α), and ratio of land to lake area (γ). Results are directly proportional to deposition rate. Precipitation, evaporation, and runoff coefficient vary in the examples considered. The table also shows the sensitivity of the land area/lake area ratio. Results are approximately proportional to α when $\alpha\gamma$ is large. For smaller values of the product, the results are less sensitive to values of α .

Table 6 shows that, for an α of 0.1, concentration increases in lakes in the eastern United States would be less than about 0.005 $\mu\text{g/L}$ for a deposition rate of 10 $\mu\text{g/m}^2/\text{yr}$. Results are fairly insensitive to the land/water ratio in that region. If the ratio was 100, trace-element concentrations would decrease by a factor of about five if α decreased from 0.1

Table 6 Trace-Element Concentration Increases in a Lake Receiving Inputs from Atmospheric Deposition^a

U.S. Location ^b	Precipitation ^c (m/yr)	Evaporation ^c (m/yr)	Annual Runoff Coefficient ^c	Increase in Concentration ^d (µg/L)		
				Y = 1000	Y = 100	Y = 10
Northwest	1.6	0.60	0.67	0.009	0.001	0.002
Northeast	1.0	0.66	0.60	0.002	0.002	0.003
Southeast	1.2	1.1	0.30	0.003	0.003	0.005
Ohio Basin	1.0	0.86	0.40	0.002	0.003	0.005
South Central	0.76	1.5	0.10	0.01	0.02	e
West	0.50	1.1	0.50	0.04	0.06	e
Northern Great Plains	0.41	0.81	0.013	0.2	1	e
Northern Great Plains	0.41	0.81	0.063	0.04	0.05	e

^aBasis for calculations: The lake has a net outflow; annual inflow exceeds evaporation loss. The lake is in equilibrium with atmospheric and tributary inputs. Atmospheric deposition rate of the trace element is assumed to be 10 µg/m²/yr. Other inputs are neglected. No trace elements from the water column are lost to sediments or to the atmosphere. Ten percent of the trace elements deposited on land are transported to the lake.

^bLocations were chosen to illustrate regional differences and do not represent any particular sites in the areas indicated.

^cPrecipitation and evaporation estimates (for shallow lakes) were taken from Linsley, Kohler, and Paulhus, (1975). Runoff coefficient was estimated using the ratio of annual runoff to annual precipitation. Annual runoff estimates were also taken from Linsley et al. (1975).

^dy is the ratio of terrestrial area in the watershed to the surface area of the lake. Results are rounded to one significant figure.

^eEvaporative loss exceeds input to the lake for Y = 10.

to 0.01. Results would increase if wet deposition were included, but similar order of magnitude results would be expected.

Compared to the criteria summarized in the appendix, this result is orders of magnitude less than any criteria for freshwater life except those for Hg and Cd. Results are about two orders of magnitude less than the criteria for Cr^{+6} . The value of $0.005 \mu\text{g/L}$ is comparable to the criterion for Cd ($0.025 \mu\text{g/L}$ with a hardness of 100 mg/L as CaCO_3) and well above the criterion for Hg ($0.00057 \mu\text{g/L}$), all for 24-h averages. Although wet deposition is not considered, the results should still be conservative since the model assumes no loss to sediments and all material present is in a recoverable form. The only concerns for aquatic life in most eastern lakes should be for Hg and possibly for Cd (again from a single power plant). Human health concerns would not be significant.

In more arid western areas, concentration increases have the potential for being larger. This is due to higher rates of evaporation from the lake (relative to precipitation) and lower runoff coefficients. The results in the West are also more sensitive to the ratio of land area to water area. As evaporative loss approaches input to the lake, the model becomes less appropriate. The closed-basin model is probably of more value in such cases.

In the West, estimated concentration increases can reach $1 \mu\text{g/L}$ in some cases (even when $\gamma = 100$). In those cases, Cd, Cr, Hg, and Pb concentrations may approach or exceed criteria for aquatic life. Copper may also be a concern (assuming deposition rates comparable to those for other trace elements) since it has a 24-h limit of $5.6 \mu\text{g/L}$ for freshwater life. The increases are equivalent to about 10% of the human health and drinking-water criteria for Cd, Cu, and Se and exceed those criteria for Hg. The $10 \mu\text{g/m}^2/\text{yr}$ deposition rate probably exceeds the deposition rates for all elements discussed except Zn. The concentration increases are probably overestimates since losses to sediments were neglected and since all material is assumed to be recoverable. The calculations also assume evaporation from a shallow lake; for deeper lakes, the evaporation would be less and the concentration increase lower. Nevertheless, this assessment indicates that trace elements may be a concern in some western lakes, in the following order: $\text{Hg} > \text{Cd} > \text{Cr} > \text{Pb} > \text{Cu} > \text{Ni}, \text{Se}$. (Note again the limited ability of the analysis to assess effects related to Hg.)

In a lake that has no outlet and that retains all trace elements in the water column, concentration will increase indefinitely and all criteria will be violated eventually. Assume a depth of 1 m (a shallow lake) and a time period of 40 yr, about the lifetime of a power plant. If export of trace elements from the watershed is 10%, the ratio of land area to water area is 100, and the deposition rate is $10 \mu\text{g/m}^2/\text{yr}$, trace-element concentration will increase $4.4 \mu\text{g/L}$ after 40 years. As the discussion for lakes with an outlet indicates, such an increase would be significant for numerous trace elements, including Cd, Cr, Cu, Hg, Ni, Pb, Se, and Zn. If the average depth were 10 m and the export from the land were 1%, then the estimated concentration increase would be $0.08 \mu\text{g/L}$, indicating the potential for problems with only Hg, Cd, and Cr. The results are sensitive to the depth of the lake and the product $\alpha\gamma$. Again, no losses to sediments were considered and all material was assumed to be recoverable.

The discussion above is based on a $10 \mu\text{g}/\text{m}^2/\text{yr}$ deposition rate. As already pointed out, this rate equals or exceeds the typical and maximum deposition rates calculated (see Table A.2) for the two coals and sites considered, except for Zn at the eastern site. Meteorological conditions (e.g., because of effects of terrain) might exist in some locations that would cause deposition to be focused in a small area. If such focusing produced an order-of-magnitude increase in deposition (to $100 \mu\text{g}/\text{m}^2/\text{yr}$), the rate of trace-element accumulation would exceed that obtained (except for Pb and Zn) if all deposition were uniformly distributed within 50 km of the source, based on Table A.2. Even with this much-increased rate, the conclusions reached above would not change dramatically. The same group of trace elements would be of most concern and in the same order. No problem would be projected for As, Ba, or Mn (no criteria are specified for Co and V). However, drinking-water criteria for Cd and Se could be approached under worst-case conditions. The possibility of exceeding the aquatic-life criteria for Cu and Pb would be increased. Localized conditions that produce enhanced deposition could, therefore, increase the likelihood of problems.

Several situations have been examined. A conservative approach that overestimates impacts was used and only a single, modern, coal-fired power plant was considered. The following conclusions can be drawn about the effects on water quality of atmospheric deposition of trace-element emissions. First, for streams, no problems related to human health are anticipated, except possibly for Hg in arid areas. Adverse effects on aquatic life from Hg and Cd might occur in some streams during wet weather. Second, for lakes, any effects would occur primarily in arid areas and in shallow lakes. Worst-case conditions in such cases could result in significant concentration increases for many elements. Primary concern would be for Hg and Cd. (Again, the model assumed no loss of material to sediments. Sedimentation would decrease the magnitude of estimated impacts. Certain meteorological conditions or changes in atmospheric chemistry might increase deposition of some elements in certain areas. Any such change would increase the potential for adverse effects.) All elements were assumed to be associated with particles in the atmosphere. Mercury exists primarily as a vapor; therefore, the deposition rates estimated for Hg are probably not very accurate. However, the very low levels of Hg required to exceed criteria, and the fact that Hg emissions are comparable to emissions for other elements (see appendix) suggests a need for concern. It is worth noting that, while climatic conditions suggest the largest potential for problems is in arid areas of the West, western coal has a lower trace-element content in general than eastern coals, partially offsetting the potential for problems to occur.

Many workers have assessed the water-quality effects of atmospheric emissions from the energy sector. These efforts include field observations as well as more general assessments. Impacts vary since so many factors are involved that can influence environmental concentrations of the trace elements. For emissions from coal-fired plants, these factors include coal type, particulate control, stack height, atmospheric conditions, mode of deposition, and pollutant behavior once the substances reach the surface. Impact is also a function of how sensitive a particular region is to atmospheric inputs of trace elements. This sensitivity varies also; it depends on the importance of atmospheric inputs to aquatic trace-element budgets in the region, existing background concentrations of the elements and other constituents in water, hydrological conditions, and the presence of sensitive species. All these

factors involving source, transport, and sensitivity imply the possibility of wide ranges in the significance of potential impacts. Field studies have examined only a limited number of situations. At least for Lake Michigan, evidence suggests that atmospheric inputs are important and some potential may exist for problems in that region.

Further field studies are needed to better define problems in various locations, particularly in the West. Improved trace-element budgets for watersheds must be developed so that watershed retention of trace elements can be better quantified as a function of element, watershed character, and, possibly, time.

More realistic assessments that consider the removal of trace elements to sediments and possible problems of toxicity in sediments should be conducted, especially for the trace elements most likely to produce adverse effects. Such assessments should consider regional differences and perhaps the effects of enhanced deposition in small areas due to meteorological conditions. The effects of wet deposition should be considered explicitly where appropriate. The analysis of effects due to Hg should consider appropriate mechanisms for removal from the atmosphere. Proper assessment may first require additional experimental effort. The effects of atmospheric inputs on the trace-element budgets of various aquatic systems should also be examined. The effects of atmospheric emissions and other waste streams from power plants should be considered together in an integrated assessment of the trace-element problem. Such an evaluation is given in a separate report (Davis, 1981). Effects may involve moderate increases in background concentrations, so chronic effects may be more important than acute ones, although both should be considered. On the basis of the observations and assessments described above, the probability of dramatic impacts on the aquatic environment due to atmospheric inputs of trace elements released from coal-fired power plants seems low. However, the potential for more subtle, long-term effects in certain areas should not be ignored.

2.5 REFERENCES FOR SECTION 2

Anderson, W.L., and K.E. Smith, Dynamics of Mercury at Coal-Fired Power Plant and Adjacent Cooling Lake, Environmental Science and Technology, 11(1):75-80 (1977).

Andren, A.W., D.H. Klein, and Y. Talmi, Selenium in Coal-Fired Steam Plant Emissions, Environmental Science and Technology, 9(9):856-858 (1975a).

Andren, A.W., and S.E. Lindberg, Atmospheric Input and Origin of Selected Elements in Walker Branch Watershed, Oak Ridge, Tennessee, Water, Air, and Soil Pollution, 8:199-215 (1977).

Andren, A.W., S.E. Lindberg, and L.C. Bate, Atmospheric Input and Geochemical Cycling of Selected Trace Elements in Walker Branch Watershed, Oak Ridge National Laboratory Report ORNL-NSF-EATC-13 (1975b).

Benninger, L.K., D.M. Lewis, and K.K. Turekian, The Use of Natural Pb-210 as a Heavy Metal Tracer in the River-Estuarine System, Marine Chemistry in the Coastal Environment, T.M. Church, ed., American Chemical Society Symposium Series 18, American Chemical Society, Washington, D.C. (1975).

Committee on Lead in the Human Environment, Lead in the Human Environment, National Academy of Sciences, Washington, D.C. (1980).

Crockett, A.B., and R.R. Kinnison, Mercury Residues in Soil Around a Large Coal-Fired Power Plant, Environmental Science and Technology, 13(6):712-715 (1979).

Davis, M.J., Effects of Energy Development on Regional Surface-Water Quality, U.S. Department of Energy draft report (1981).

Dolske, D.A., and H. Sievering, Trace Element Loadings of Southern Lake Michigan by Dry Deposition of Atmospheric Aerosol, Water, Air, and Soil Pollution, 12:485-502 (1979).

Dvorak, A.J., et al., The Environmental Effects of Using Coal for Generating Electricity, U.S. Nuclear Regulatory Commission Report NUREG-0252 (1977).

Eisenreich, S.J., Atmospheric Input of Trace Metals to Lake Michigan, Water, Air, and Soil Pollution, 13:287-301 (1980).

Evans, D.W., J.G. Wiener, and J.H. Horton, Trace Element Inputs from a Coal Burning Power Plant to Adjacent Terrestrial and Aquatic Environments, J. Air Pollution Control Assn., 30(5):567-573 (1980).

Federal Register, 45:79318 (Nov. 28, 1980a).

Federal Register, 45:79322 (Nov. 28, 1980b).

Klein, D.H., et al., Pathways of Thirty-Seven Trace Elements Through Coal-Fired Power Plant, Environmental Science and Technology, 9(10):973-979 (1975).

Klein, D.H., and P. Russell, Heavy Metals: Fallout Around a Power Plant, Environmental Science and Technology, 7(4):357-358 (1973).

Lantzy, R.J., and F.T. Mackenzie, Atmospheric Trace Metals: Global Cycles and Assessment of Man's Impact, Geochimica et Cosmochimica Acta, 43:511-525 (1979).

Lindberg, S.E., et al., Mechanisms and Rates of Atmospheric Deposition of Selected Trace Elements and Sulfate to a Deciduous Forest Watershed, Oak Ridge National Laboratory Report ORNL/TM-6674 (1979).

Lindberg, S.E., Mercury Partitioning in a Power Plant Plume and Its Influence on Atmospheric Removal Mechanisms, Atmospheric Environment, 14:227-231 (1980).

Lindberg, S.E., and R.C. Harriss, Trace Metal Solubility in Aerosols Produced by Coal Combustion, Environmental and Climatic Impact of Coal Utilization, J.J. Singh and A. Deepak, eds., Academic Press, New York (1980).

Linsley, R.K., Jr., M.A. Kohier, and J.L.H. Paulus, Hydrology for Engineers, 2nd Ed., McGraw-Hill, New York (1975).

- Lyon, W.S., Trace Element Measurements at the Coal-Fired Steam Plant, CRC Press, Cleveland (1977).
- Muhlbaier, J., and G.T. Tisue, Cadmium in the Southern Basin of Lake Michigan, Water, Air, and Soil Pollution, 15:45-59 (1981).
- Nriagu, J.O., Global Inventory of Natural and Anthropogenic Emissions of Trace Metals to the Atmosphere, Nature, 279:409-411 (1979).
- Prosi, F., Heavy Metals in Aquatic Organisms, Metal Pollution in the Aquatic Environment, U. Forstner and G.T.W. Wittman, eds., Springer-Verlag, Berlin (1979).
- Siccama, T.G., and W.H. Smith, Lead Accumulation in a Northern Hardwood Forest, Environmental Science and Technology, 12(5):592-594 (1978).
- Smith, W.H., and T.G. Siccama, The Hubbard Brook Ecosystem Study: Biogeochemistry of Lead in the Northern Hardwood Forest, Journal of Environmental Quality, 10(3):323-333 (1981).
- Turner, R.R., S.E. Lindberg, and K. Talbot, Dynamics of Trace Element Export from a Deciduous Watershed, Walker Branch, Tennessee, Watershed Research in North America, Vol. II, D.L. Correll, ed., Chesapeake Bay Center for Environmental Studies, Smithsonian Institution, Edgewater, Md., pp. 661-680 (1977).
- U.S. National Committee for Geochemistry, Panel on the Trace Element Geochemistry of Coal Resource Development Related to Health, Trace-Element Geochemistry of Coal Resource Development Related to Environmental Quality and Health, National Academy Press, Washington, D.C. (1980).
- Van Hook, R.I., W.F. Harris, and G.S. Henderson, Cadmium, Lead, and Zinc Distributions and Cycling in a Mixed Deciduous Forest, Ambio 6(5):281-286 (1977).
- Vaughan, B.E., et al., Review of Potential Impact on Health and Environmental Quality from Metals Entering the Environment as a Result of Coal Utilization, Battelle/Pacific Northwest Laboratory Report NP-20585 (1975).
- Wagenet, R.J., W.J. Grenney, and J.J. Jurinch, Environmental Transport Model of Heavy Metals, American Society of Civil Engineers, J. of Environmental Engineering Division, pp. 61-76 (Feb. 1978).
- Walther, E.G., Predicted Transport of Air Pollutants from the Navajo and Kaiparowits Generating Stations into Lake Powell, available from National Technical Information Service as PB-265-101 (1976).
- Wangen, L.E., and M.D. Williams, Elemental Deposition Downwind of a Coal-Fired Power Plant, Water, Air, and Soil Pollution, 10:33-44 (1978).
- Wiener, J.G., Aerial Inputs of Cadmium, Copper, Lead, and Manganese into a Freshwater Pond in the Vicinity of a Coal-Fired Power Plant, Water, Air, and Soil Pollution, 12:343-353 (1979).

3 EFFECTS OF ACID PRECIPITATION

3.1 BACKGROUND

Pure water in equilibrium with carbon dioxide (CO_2) has a pH of 5.65. Rainfall in equilibrium with atmospheric CO_2 would be expected to have this pH. However, precipitation in large portions of North America (particularly the Northeast) and Scandinavia has pH values well below this level. Such precipitation is often labeled acidic. Potential effects of acid precipitation include damage to the aquatic environment, deterioration of materials (masonry, especially limestone or marble; metals; organic materials), and adverse effects on soils and possibly on vegetation (direct effects have been demonstrated under experimental, but not field, conditions). The low pH of rainfall is due principally to sulfuric and nitric acids. Various workers have suggested that these acids result largely from oxides of sulfur (SO_x) and nitrogen (NO_x) that are released when fossil fuels are burned for power generation and other uses (e.g., Likens, 1976).

In this discussion, the term "acid precipitation" includes both wet and dry deposition of hydrogen ions (H^+) and associated anions [sulfate (SO_4^{-2}) and nitrate (NO_3^-)]. Wet deposition includes those processes in which substances are scavenged by precipitation and carried to the surface contained in precipitation. Dry deposition includes gravitational settling of particles, aerosol impaction, and sorption of gases at the surface. Both wet and dry deposition are important processes that must be included in any estimate of watershed inputs. Both types of deposition have the potential to produce similar aquatic impacts. Their effects are the same if deposition occurs over a body of water.

Establishing a quantitative cause-and-effect relationship between the production of SO_x and NO_x and acid precipitation is a difficult problem. There are some gaps in our ability to quantitatively relate atmospheric releases of SO_x and NO_x to their deposition downwind. Considerable evidence, however, suggests that acid precipitation in the northeastern United States, eastern Canada, and Scandinavia is related to emissions from large industrialized regions upwind from these areas.

Energy-related sources of acid precursors are considered significant contributors to the acidity in low-pH rainfall, although the degree of contribution is unquantified. This report assumes that such sources can contribute atmospheric inputs of acids to watersheds and it focuses on aquatic effects. Sources, transport, and transformation of pollutants before reaching the land or water surface are not discussed here. Basic references are cited in the text and given in the bibliography, however, so the interested reader can pursue these related topics further.

Rainfall with particularly low pH is observed in the northeastern United States, in eastern Canada, and in portions of Scandinavia. In the northeastern U.S., pH values are often below 4.5; precipitation appears to be most acid from May to September, and least acid in winter (December to February) (Hornbeck et al., 1977). Acid precipitation occurs in other portions of the United States as well. Brezonik et al. (1980) report average pH values below 4.7 over the northern three-quarters of Florida for 1978-1979.

The annual deposition of hydrogen ions there is about one-third to one-half of that in the Northeast.

Liljestrand and Morgan (1979) report a volume-weighted average pH of 4.06 for Pasadena, California, in 1976 and 1977. Lewis and Grant (1980) observed acid precipitation in Colorado, and noted a trend toward decreased pH in the region during 1975-1978. They obtained an average pH of 4.63 for the last year of data collected.

The pH of precipitation can vary from storm to storm and both spatially and temporally within storms. It has been suggested that there is a general trend toward increased acidity in precipitation in recent times and also a trend toward more acid precipitation over wider areas (Likens et al., 1979; Likens and Butler, 1981). However, some workers have questioned the presence of these long-term trends because of the nature of some of the early measurements (cf. GCA Corp., 1981).

3.2 AQUATIC EFFECTS OF ACID PRECIPITATION

3.2.1 Introduction

The deposition of acids from the atmosphere can result in a variety of effects in the freshwater environment. Acids may reach a watershed in precipitation (rain or snow) or in dry deposition, and may be delivered directly to a body of water or to its drainage basin. Hydrogen ions deposited directly on a body of water may reduce the alkalinity of the body of water and depress pH (which, in turn, may have chemical and biological consequences and further modify water quality). The acids deposited on land will generally participate in more complex processes in the soil (Gorham and McFee, 1980; Last et al., 1980; Ulrich, 1980). The H^+ that is deposited or produced by other constituents in the precipitation may be buffered by reactions in the soil. A substantial fraction of H^+ may not reach the aquatic environment. If calcium or magnesium carbonates are present, H^+ will be consumed and bicarbonate and calcium or magnesium will be released. When no free bases are present, but the soil has a significant cation exchange capacity*, H^+ may be exchanged for metal cations. Some H^+ may react with silicates or other minerals in the soil, releasing metal cations. Hydrogen ions that remain after ion exchange and mineral weathering will reach the aquatic environment along with leached metal cations and mobile anions, usually sulfate. The fraction of atmospheric input that reaches a body of water unchanged by contact with soil is usually small (Overrein et al., 1980; Seip, 1980a). Since, in most cases, only a relatively small fraction of acid precipitation is deposited directly on a water body, most inputs are usually influenced by soil processes.

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*Many small soil particles have a net negative charge. This charge is balanced by cations located near the surface of the particles. These ions are called exchangeable cations and the quantity (usually given in meq/100g of dry soil) is called the soil's cation exchange capacity (CEC).

In addition, the actual manner in which water moves through a watershed influences the potential for acidification, since it determines the degree of interaction between atmospheric inputs and soil. Large surface runoff will decrease the opportunity for interaction.

When ions are transported, electrochemical neutrality requires that equivalent amounts of cations and anions move together. Therefore, the transport of H^+ or metal cations from the soil to the aquatic environment requires the presence of mobile anions. Acid precipitation provides sulfate and nitrate as major anions. Nitrate tends to be retained in the soil-plant system of the catchment (Abrahamsen and Dollard, 1979; Overrein et al., 1980). Sulfate ions, on the other hand, are usually quite mobile (Overrein et al., 1980), although sulfate retention varies with soil type, depending on the amount of hydrous oxides of iron and aluminum present (Johnson, 1980; Abrahamsen and Dollard, 1979). Norwegian studies show that the increased concentrations of cations (including H^+), which are the result of increased sulfate concentrations in runoff, can explain a substantial part of the observed acidification of fresh water (Overrein et al., 1980). Observations in a number of North American watersheds have also shown little retention of sulfate in the watersheds; sulfate tends to be the anion that balances cation transport in runoff (cf. Impact Assessment Work Group, 1981b). Some soils may retain sulfate; however, in many watersheds sulfate can be considered a relatively conservative anion. Additional effects of acid inputs to the catchment include nutrient leaching from soils, which reduces productivity, and mobilization of aluminum (Al), which may cause toxic effects on aquatic biota. Acids in rainfall may influence biological activity in the watershed, and, therefore, affect the movement of other chemicals. Synergistic or antagonistic effects involving co-contaminants are also possible.

Just as the character of acid rainfall varies with location, the manner in which aquatic environments respond to inputs of acid varies also. As the above discussion suggests, the principal factor that determines the response to acid inputs is the nature of bedrock, overburden, and soils in the basin. Different materials have different levels of acid-neutralizing capability and retain different quantities of the mobile anions; they consequently have different responses to acid inputs. The rocks and soils in the basin also determine to a large degree the chemical characteristics of water in the basin. A basin whose terrestrial portion provides substantial acid-neutralizing capability will tend to have water bodies with similar neutralizing characteristics.

Large concentrations of H^+ in an aquatic system can affect biota severely. In addition, since the chemical form of many toxic heavy metals is pH dependent, and since solubility is a function of species, the mobilization of toxic metals from sediments depends on the concentration of hydrogen ions, $[H^+]$. Acid rainfall contributes H^+ to an aquatic system, either directly or in runoff; therefore, the factors determining $[H^+]$ in the system are very important in determining how the system responds to acid inputs.

The alkalinity of water is a measure of its capacity to neutralize acids. Alkalinity may be thought of as a sink for H^+ . A buffer is a substance that resists changes in the concentration of H^+ . In most surface waters, buffering is provided by the carbonate system. Other sinks for

H^+ may be present, but the carbonate system usually dominates. In such cases, alkalinity is defined as:

$$[ALK] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

where

$[HCO_3^-]$ = bicarbonate concentration,

$[CO_3^{2-}]$ = carbonate concentration, and

$[OH^-]$ = hydroxide concentration

If other proton acceptors are present, their concentrations are added to the above expression. At the pH of most natural waters, the bicarbonate ion provides most of the alkalinity of the system. Carbonate minerals in the catchment area provide an important source of bicarbonate ion. In areas containing limestone, calcareous sandstones, or chalk, bicarbonate alkalinities may be substantial. Carbonate materials or aluminum and iron hydroxides and silicates in the catchment area will tend to neutralize runoff before it reaches a body of water, as already noted.

3.2.2 Water-Quality Effects of Acid Precipitation

Acid delivered directly to a body of water may lower pH. The degree of change depends on the character of the input and the buffering provided by the water. Acid deposited on the land surface may be neutralized in varying degrees by the minerals present.

Johnson (1979) found that, even in a watershed with chemically unreactive bedrock, strong acids in rainfall can be 75% neutralized in the soil by reaction with aluminum salts and biological matter. His work in New England indicates that acid rain will primarily affect water quality of lower-order streams. If carbonate materials are present in the catchment, neutralization should occur rapidly and few effects will be observed. Since impacts tend to be in low-order streams, acidification of lakes will occur more at high elevations, where most water inputs are from such sources. Acid rainfall on noncalcareous watersheds will increase concentrations of dissolved aluminum in streams and lakes due to leaching (Cronan and Schofield, 1979; Johnson, 1979.) Increased aluminum concentration may contribute to fish mortality.

Except in areas with industrial or municipal sources of pollution, the chemistry of water bodies is usually determined primarily by substances carried into the water in runoff. (An exception is lakes that occupy large fractions of their watersheds, for which precipitation provides important chemical inputs). When acid precipitation falls on a catchment area, the character of the runoff is modified. The most important effects are lower pH (in areas lacking adequate buffering) in lower-order streams, and increased concentration of toxic aluminum.

For acid input directly to a body of water, the primary concern involves change in pH. The pH of acid rainfall is generally less than that of the water body, unless the latter is quite acidified. The acid-neutralizing

capacity of the water, generally provided by bicarbonate, tends to maintain a constant pH. But as more H^+ is added, bicarbonate is eliminated. Under such circumstances, the poorly buffered lake will have declining pH (although relatively large pH fluctuations due to biological activity may occur). As bicarbonate concentration decreases, sulfate from the acid rain will replace bicarbonate as the major anion. Lower pH may increase concentrations of soluble heavy metals released from sediments.

Inputs of H^+ to a body of water are episodic. For wet deposition, this is obvious. Even for dry deposition, actual inputs to water bodies are most frequent during wet weather when materials are moved in runoff. For inputs in snow, delivery of H^+ to the aquatic environment occurs during snowmelt. The contaminants in the snowpack are delivered with the snow or in dry deposition. The contribution from dry deposition in snow-covered areas is not large, because of the low deposition velocities on snow surface (cf. Overrein et al., 1980). When snowmelt occurs, the initial meltwater is the most contaminated because pollutants are contained in the intercrystalline brines, which are the first to be washed out (Gorham, 1976). Contaminants in the first meltwater may have concentrations of five, or in extreme cases 10, times the concentration in bulk snow (cf. Overrein et al., 1980; Seip, 1980b). Studies have shown that even during snowmelt conditions, the composition of runoff is influenced by its contacts with soil and vegetation in the watershed (Overrein et al., 1980). The pH of runoff appears to be related principally to the presence of mobile anions, the nature of the soil, and the flow pattern. The mobile anions are primarily sulfate, but nitrate is a more important anion during snowmelt than at other times, when it is taken up by vegetation. However, nitrate concentration can be negligible in stream-flow even during snowmelt (Overrein et al., 1980). During the early phases of snowmelt or during a heavy rainfall with low pH, poorly buffered surface waters can undergo a rapid decrease in pH and remain acidic for a short period. This sudden decrease can result in stress on biota and could produce fish kills (Holden, 1979). Examples of rapid and substantial pH drops associated with snowmelt are given by Dickson (1980) and Schofield (1980). In both cases the initial pH was near 7, indicating that the body of water was not acidified. However, the shock events associated with snowmelt produced short-term changes in water quality that are lethal to fish. Mobilization of toxic forms of aluminum also influence the stress on fish at such times. Much of the total annual export of H^+ from a watershed may occur during a short period of spring snowmelt (Impact Assessment Work Group, 1981a).

The Electric Power Research Institute (EPRI) is sponsoring studies of three Adirondack Mountain lakes. These lakes are located close together, receive similar inputs of acid precipitation, but exhibit different chemical responses. One lake is buffered, with pH near 7, one has pH of from 4.5 to 5.5, and one has variable pH ranging from 4.5 to 7. The EPRI studies are attempting to understand the differences in responses through field studies and a mathematical modeling effort (Chen and Gherini, 1979).

3.2.3 Ecological Effects of Acid Precipitation

Acidification of a body of water may have adverse effects on the aquatic biota. For example, species may be eliminated or populations reduced.

Table 7 summarizes likely effects and Table 8 outlines effects as a function of pH.

Reduced pH generally decreases bacterial decomposition of detrital organic matter, which in turn can affect the remainder of the ecosystem in terms of energetics, nutrient cycling, and productivity at other trophic levels. In addition, species diversity is reduced as pH drops. Following the loss of bicarbonate buffering, large pH fluctuations occur. This may lead to destruction of fish populations. Fish are usually absent from waters with chronically depressed pH.

Observed effects on biota have often been correlated with changes in pH, but in many cases no cause-and-effect relationship has been established; experiments are needed to determine if effects are directly related to pH or to other factors such as increased trace-element concentrations or disruption of food chains (Impact Assessment Work Group, 1981b).

Acidification of lakes has eliminated fish populations in areas of North America and Europe. Lakes in more than 13,000 km² of southern Norway have practically no fish and populations are reduced in another 20,000 km² area (Muniz and Leivestad, 1980; Overrein et al., 1980). About 200 lakes in the Adirondacks and possibly 200 in Ontario have no fish because of acidification (Harvey, 1980). The mechanism of population extinction is usually through post-embryonic mortality and failure of recruitment of new age classes into the fish population (Harvey, 1980; Muniz and Leivestad, 1980). The death of fish in acid waters is probably because body salt regulation and normal gill function fail; aqueous aluminum compounds are important factors in upsetting the salt balance and in producing respiratory distress (Muniz and Leivestad, 1980).

Inorganic Al forms appear to be the major species involved in Al toxicity to fish (Baker and Schofield, 1980). Complexation of Al with organic compounds can reduce or eliminate the toxic effect of Al. Baker and Schofield (1980) found that, for the species of fish and range of conditions they examined, sensitivity to low pH levels decreases with increasing age and sensitivity to Al increases with increasing age. Presence of Al actually mitigated toxic effects of low pH on fish eggs. The increased Al concentrations often found in acidified lakes are potentially toxic to fish at pH levels that are otherwise not harmful (Schofield, 1980). Because sensitivity to pH and Al varies, the timing of pulses of H⁺ and Al (for example, in snowmelt) is an important factor to consider when assessing the potential effects of acidification, as is the distinction between the forms of Al present (Baker and Schofield, 1980).

3.2.4 Effects of Acid Precipitation on Drinking-Water Supply

Acidified water that serves as a source of drinking water may create problems. First, the reduced pH of the water and its lowered buffering intensity may result in a corrosive water that removes toxic metals (e.g., Pb, Cu, Zn, Cd) from the distribution system used to transport the water. Second, the water may already contain elevated concentrations of toxic metals that were leached from soils, released from sediments, or deposited from the atmosphere.

Table 7 Effect of Increased Acidity on Aquatic Biota

Bacterial decomposition is reduced and fungi dominate saprotrophic communities. Organic debris accumulates rapidly.

Ciliate fauna is greatly inhibited.

Nutrient salts are taken up by plants tolerant of low pH (e.g., mosses, filamentous algae) and by fungi.

Thick mats of these plants may develop, inhibiting sediment-to-water nutrient exchange and choking out other aquatic plants.

Phytoplankton species diversity, biomass, and production are reduced.

Species diversity and biomass of zooplankton and benthic invertebrates are reduced. Remaining benthic fauna consists of tubificids and Chironomus (midge) larvae in the sediments. Some tolerant species of stone flies and mayflies persist, as does the alderfly. Air-breathing water bugs of the order Hemiptera (waterboatman, backswimmer, water strider) may become abundant.

Fish populations are reduced or eliminated.

Source: Hendry et al. (Jan. 1980).

Table 8 Effects of Various pH Ranges on Aquatic Biota

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pH Range	Effects
8.0-6.0	Long-term changes of less than 0.5 pH units are likely to alter the biotic composition of freshwater. However, the significance of such changes is slight. A decrease of 0.5 to 1.0 pH units in the range 8.0 to 6.0 may cause detectable alterations in community composition. Productivity of competing organisms will vary. Some species will be eliminated.
5.5-5.0	Many species will be eliminated, and species numbers and diversity indices will be reduced. Crustacean zooplankton, phytoplankton, molluscs, amphipods, most mayfly species, and some stone fly species will begin to drop out. In contrast, several pH-tolerant invertebrates will become abundant, especially the air-breathing forms, those with tough cuticles that prevent ion losses, and some forms that live within the sediments. Overall, invertebrate biomass will be greatly reduced.
5.0-4.5	Decomposition of organic detritus will be severely impaired. Autochthonous and allochthonous debris will accumulate rapidly. Most fish species will be eliminated.
<4.5	All of the above changes will be greatly exacerbated, and all fish will be eliminated.

Source: Hendry et al. (Jan. 1980).

The Impact Assessment Work Group (1981a) has reviewed information on the possible contamination of drinking-water supply. They report that no clear evidence of health effects from consumption of contaminated water has been reported in the literature. However, they report several cases in which acid precipitation has produced adverse effects on drinking-water supply:

- Acidification of a New York State reservoir resulted in elevated concentrations of Pb in drinking water.
- Acidification of well water corroded household plumbing in Sweden.
- Elevated concentrations of metals were found in some Adirondack Mountain homes that use spring water and metal pipes.
- Elevated concentrations of Pb in tapwater were found in some homes that use cisterns (Clarion County, Penn.).

The areas most sensitive to possible health problems from acidified water supplies are those that have no water-treatment system, use lead in their plumbing systems, rely on cisterns for water supply, or have high levels of metals in sediments.

3.3 AREAS SENSITIVE TO ACID PRECIPITATION

Water bodies respond differently to inputs of acid from the atmosphere. That is, certain areas are more sensitive than others. Several factors determine the degree of sensitivity, some of which have already been noted. An area's sensitivity depends on:

- The character of the bedrock, overburden, and soils in the watershed. (The chemistry of water bodies is also determined primarily by geology.)
- The vegetation and the nature of land use in the basin.
- The ratio of lake area to the area of the entire catchment. The larger the ratio, the larger the direct input of acid to the lake and, hence, the larger the effect.
- The elevation of the watershed. Higher elevations receive higher inputs of acids due to the orographic increase of rainfall.

Bedrock geology is an important factor determining sensitivity to acid precipitation (unless the bedrock is covered by material of a different character, which sometimes occurs as the result of glacial action). Galloway and Cowling (1978) developed a map showing areas in North America where bedrock is igneous or metamorphic. Such bedrock would contribute little to neutralizing acid precipitation on land and should result in low alkalinities in local lakes and streams. These areas should, therefore, be sensitive to inputs of acid. Galloway and Cowling's map (Fig. 2) shows that the total sensitive area, based on bedrock characteristics, is quite large.

Hendry et al. (1980) prepared more-detailed maps of bedrock geology for the eastern United States. Their maps provide resolution at the county level. Bedrock is classified into four groups:

- I. Provides little to no buffering -- susceptible to effects of acid precipitation.
- II. Provides medium to low buffering -- acid rain will affect only first- and second-order streams and small lakes.
- III. Provides medium to high buffering -- effects are unlikely except due to overland flow on frozen ground.
- IV. Provides "infinite" buffering -- unaffected by acid precipitation.

The maps constructed by Hendry et al. (1980) indicate the fraction of bedrock represented by type I and by type II rocks. Figure 3 summarizes their results. Such maps can be used to determine regions with high sensitivity to acid precipitation but are not intended for detailed analysis of small areas. These maps were verified by comparing the sensitive areas with county maps of minimum or average surface-water alkalinities for New Hampshire and North Carolina, where good agreement was found. Figures 2 and 3 were developed by different workers using different approaches and levels of spatial resolution, so total consistency between the two should not be expected.

Kaplan et al. (1981) have stressed that soil characteristics are of major importance in determining the sensitivity of water bodies to acid precipitation. In a study of the northeastern United States, they found that soils predominate over rocks in determining regional water-quality characteristics. Their analysis showed that both rocks and soils are determinants of pH and alkalinity of surface waters, but that the presence of a large fraction of alfisol soils better indicates areas with waters having higher levels of alkalinity than does the nature of bedrock geology.

Soil sensitivity to acid precipitation also affects acid precipitation's impact on the aquatic environment. Acid inputs to soils may increase the leaching of some plant nutrients and aluminum, and may affect microbiological processes in the soil. These factors, as well as the general ability of the soil to act as a buffer, can affect water quality.

McFee (1980) examined soil sensitivity to acid precipitation and mapped areas with sensitive soils. He defines soils as being slightly sensitive if 100 cm of annual precipitation at pH 3.7 over a 25-yr period provides an acid input equal to 10-25% of the soil's cation exchange capacity in the top 25 cm of soil. This is equivalent to a soil with a CEC of 6.2 - 15.4 meq/100 g (for a soil with a density of 1.3 g/cm³). Soils are defined as sensitive if the same input exceeds 25% of the CEC in the top 25 cm (CEC < 6.2 meq/100 g). His approach is somewhat arbitrary, but it does quantify sensitivity and uses soil data that are available for large areas.

Fig. 2 Regions with Lakes that May Be Sensitive to Acid Inputs, on the Basis of Bedrock Geology [Source: Galloway and Cowling (March 1978)]

McFee (1980) devised the following sensitivity classes for soils:

1. Nonsensitive Areas. Includes: (a) soils that contain free carbonates (are calcareous) in the top 25 cm; (b) soils subject to frequent flooding; (c) soils with average CEC > 15.4 meq/100 g in the top 25 cm.
2. Slightly Sensitive Areas. These areas are not included in 1(a) or 1(b) and have an average CEC > 6.2 meq/100 g and < 15.4 meq/100 g in the top 25 cm.

Fig. 3 Bedrock Classification of the Eastern United States [Source: After Hendry et al. (Jan. 1980), as presented by Altshuller and McBean (1979)]

3. Sensitive Areas. These areas are not included in 1(a) or 1(b) and have an average CEC < 6.2 meq/100 g in the top 25 cm.

Using these definitions, McFee mapped soils of the eastern states. Figure 4 shows a general map of the eastern United States that provides a useful overview. Land-use practices, however, can completely overwhelm the effects of acid precipitation in cultivated areas where soil amendments are applied. Consequently, the soil sensitivities shown in the map apply only to noncultivated areas.

Another approach to identifying sensitive areas focuses on the chemical characteristics of the lake itself. One method relies on the calcite saturation index (CSI), which indicates the water's degree of saturation with

Fig. 4 Soil Sensitivity in the Eastern United States
[Source: After McFee (Jan. 1980)]

calcite (CaCO_3) (Kramer, 1976; Conroy et al., 1974). Water well-saturated with CaCO_3 should have a reasonable amount of buffering relative to inputs of acid. The CSI is basically the difference between the water's observed pH and its pH if saturated with CaCO_3 . It is defined by:

$$\text{CSI} = \text{pCa}^{+2} + \text{pALK} - \text{pH} + \text{pK}$$

where:

$$\text{pX} = -\log_{10}[\text{X}]$$

$$\text{pK} = 2$$

The $[Ca^{+2}]$ is in moles/L and alkalinity is in eq/L. At saturation, CSI equals zero; if supersaturated, CSI is negative, and if undersaturated, CSI is positive. Conroy et al. (1974) claim that waters with $CSI > 4$ are unstable if acid precipitation is added. A similar index is often used to assess the tendency of calcium carbonate to form linings on pipes in water-distribution systems. The CSI only provides an indication of the buffering provided by the lake. It says nothing about effects in the watershed.

Hendriksen (1979) developed an empirical approach for identifying acidified lakes. His method plots pH and calcium concentration (less calcium of sea-spray origin). Figure 5 shows plots of pH and $[Ca]$ for lakes in northern and northwestern Norway (closed circles) and in southern and south-eastern Norway (open circles). Southern Norway receives highly acid precipitation. Figure 6 shows similar plots for Sweden. The open circles are for southern Sweden and the closed circles are for west-central Sweden. Rainfall in southern Sweden is acidic. Hendriksen found that the empirical curve that separates acidified and nonacidified lakes is the same in both areas of Scandinavia, and that the curve appears to hold in North America. The curve is useful since it indicates lakes that have lost some alkalinity but have a pH high enough to still be safe for aquatic life. In Hendriksen's words, the indicator provides an "early warning." His basis for considering the $[Ca]$ -pH plots is that, in unacidified lakes, bicarbonate alkalinity is present in concentrations equivalent to the sum of magnesium and calcium concentrations (less inputs from sea spray). Since the Ca/Mg ratio is approximately constant, and since pH is related to current alkalinity and acidity, the plots should distinguish between acidified and unacidified water. Where calcium and bicarbonate concentrations are not proportional or where calcium and bicarbonate are not the principal cation and anion in natural conditions, the approach is not appropriate.

Hendriksen defines acidification of lakes as:

acidification = pre-acidification alkalinity - present-day alkalinity

Operationally, use of this definition presents a problem since few data are available to define preacidification alkalinities. Hendriksen shows a way to estimate these alkalinities from present-day calcium concentrations, since calcium and alkalinity concentrations are proportional in soft, oligotrophic lakes that are not acidified. For a group of 59 lakes in northern and northwestern Norway, he found that alkalinity = $-29 + 1.32[Ca]$ ($r^2 = 0.85$), where the concentrations are in eq/L. For a similar group of 98 lakes in Canada, he found alkalinity = $-32 + 1.42[Ca]$ ($r^2 = 0.76$). This approach assumes that calcium concentrations do not increase while a lake is being acidified, or that if they do change, then an equivalent amount of alkalinity is added to the lake and then is consumed by acidification.

In more recent work, Hendriksen (1980) developed an empirical model that predicts lake pH and fish population status on the basis of precipitation pH and lake calcium concentration. His model is intended for use in areas with thin soils, with bedrock that provides little buffering, and with soft and poorly buffered surface waters. He bases the approach on the hypothesis that acidification can be considered as a titration of a bicarbonate solution with strong acids. His analysis is based on 719 lakes in southern Norway.

Fig. 5 pH and Calcium Concentrations in Lakes in Northern and Northwestern Norway (●) and Southern and Southeastern Norway (○)
[Source: After Hendriksen (April 1979)]

Hendriksen's approach to developing the model is basically as follows. The pH of lakewater is a function of the lake's original alkalinity and the quantity of H^+ added by strong acids. The original alkalinity of a lake is related to its present nonmarine (i.e., corrected for sea spray) calcium concentration. The quantity of H^+ added by strong acids is related to the nonmarine sulfate concentration in the lake (see discussion below on nitric acid inputs). Regression analysis shows that nonmarine sulfate concentration is linearly related to the pH of precipitation. Regressions can be made of calcium concentrations (equivalent to original alkalinity) on nonmarine sulfate concentration for groups of lakes within narrow pH intervals. Lakes with $pH > 5.3$ are bicarbonate-dominated and have good fish populations. Those with $pH < 4.7$ are acid and have sparse or no fish populations. Lakes in

Fig. 6 pH and Calcium Concentrations in Lakes in Southern (o) and West-Central Sweden (•) [Source: After Hendriksen (April 1979)]

the pH interval 4.7 to 5.3 are transition lakes. The regression of calcium concentrations on nonmarine sulfate concentrations for lakes with pH values near 4.7 and 5.3 yields Fig. 7, in which nonmarine sulfate concentration is converted to rainfall pH using the regression relation between the two variables.

Figure 7 predicts lake status as being bicarbonate, transition, or acid, given the pH of rainfall and the nonmarine calcium concentration of a lake. Decreased pH of rainfall will result in a horizontal movement across the figure. The ordinate of the figure represents the geological influences on the lake, since calcium concentration is related to bedrock geology of the catchment. The abscissa represents the influence of precipitation. To the left of the transition zone, geology dominates; to the right, precipitation does.

Fig. 7 A Nomograph to Predict Lake pH and Fish Population Status Given Nonmarine Calcium Concentration and Precipitation pH [Source: After Hendriksen (March 1980).]

Hendriksen used the model to accurately predict pH values for an independent set of lakes in southern Norway. Hendry et al. (1980) used the approach to predict pH and fish population status for 214 Adirondack Mountain lakes, as well as for a group of lakes in Canada. They correctly classified 70% of the Adirondack lakes and correctly designated 98% of the Canadian lakes as bicarbonate lakes.

The U.S. Environmental Protection Agency (EPA) is supporting further work by Hendriksen to investigate the model's applicability to lakes in North America and to study its use as a predictor of changes in pH and fish status due to acid inputs (Cowling and Linthurst, 1980). Questions under consideration include how calcium concentration may vary with acid inputs and how to model the effects of nitrate ion in areas where sulfate and nitrate are both important anions.

In summary, several approaches are available for identifying regions or individual bodies of water that may be susceptible to acid inputs. The methods that involve bedrock and soils assess the regional potential for problems in the aquatic environment, should acid precipitation be present. The approaches that involve water chemistry assess the susceptibility of particular lakes to acid inputs. Hendriksen's work quantifies the degree of acidification that may have occurred already.

The preceding discussion on sensitive areas relates primarily to lakes. Approaches are also needed for streams and ground water. Limited information is available on the effects of acid precipitation on ground water, but they may exist in some areas. As noted in the text, impacts from acid precipitation do occur in some streams; such effects are associated with snowmelt or other events that flush H^+ into the streams.

If aquatic resources are to be protected from adverse effects of acid precipitation, then it is necessary to know what levels of inputs produce what effects in different aquatic systems. Estimates of the level of inputs that can be accepted without producing additional negative effects must be available, and the location of the most sensitive resources must be known. Any rational strategies for controlling inputs will make use of such information. Control strategies must also consider the relative importance of nitrate and sulfate in influencing the aquatic environment.

Acid precipitation is currently a very active area of study; the literature is growing rapidly. This section provides a review of some major topics involving acid precipitation and its aquatic effects as of mid-1981.

3.4 REFERENCES FOR SECTION 3

Abrahamsen, G., and G.J. Dollard, Effects of Acid Precipitation on Forest Vegetation and Soil, Ecological Effects of Acid Precipitation, Workshop Proc., Electric Power Research Institute Report EA-79-6-60, Palo Alto, Cal. (1979).

Altshuller, A.P., and G.A. McBean, The LRTAP Problem in North America: A Preliminary Overview, prepared by the United States - Canada Research Consultation Group on the Long-Range Transport of Air Pollutants, Canadian Embassy, Washington, D.C. (1979).

Baker, J.P., and C.L. Schofield, Aluminum Toxicity to Fish as Related to Acid Precipitation and Adirondack Surface Water Quality, Proc. International Conf. on the Ecological Impact of Acid Precipitation, D. Drablos and A. Tollan, eds., SNSF Project, P.O. Box 61, 1432 Ås-NH, Norway pp. 75-83, (1980).

Brezonik, P.L., E.S. Edgerton, and C.D. Hendry, Acid Precipitation and Sulfate Deposition in Florida, Science, 208:1027-1029 (May 1980).

Chen, C.W., and S. Gherini, Modeling the Lake Acidification Process, Ecological Effects of Acid Precipitation, Workshop Proc., Electric Power Research Institute Report EPRI EA-79-6-LD, Palo Alto, Cal. (1979).

Conroy, N., D.S. Jeffries, and J.R. Kramer, Acid Shield Lakes in the Sudbury, Ontario, Region, Water Pollution Research in Canada 1974, 9:45-61 (1974).

Cowling, E.B., and R.A. Linthurst, Research on Effects of Acid Precipitation on Aquatic and Terrestrial Ecosystems, U.S. Environmental Protection Agency - North Carolina State University Acid Precipitation Program, First Annual Report, Raleigh, N.C. (1980).

Cronan, C.S., and C.L. Schofield, Aluminum Leaching Response to Acid Precipitation: Effects on High Elevation Watersheds in the Northeast, Science, 204:304-305 (April 1979).

Dickson, W., Properties of Acidified Waters, Proc. International Conf. on the Impact of Acid Precipitation, D. Drablos and A. Tollan, eds., SNSF Project, P.O. Box 61, 1432 Ås-NLH, Norway, pp. 75-83 (1980).

Galloway, J.N., and E.B. Cowling, The Effects of Precipitation on Aquatic and Terrestrial Ecosystems: A Proposed Chemistry Network, J. Air Pollution Control Assn., 28(3):229-235 (March 1978).

GCA Corporation, Acid Rain Information Book, U.S. Department of Energy Report DOE/EP-0018 (1981).

Gorham, E., Acid Precipitation and Its Influence upon Aquatic Ecosystems - An Overview, Water, Air, and Soil Pollution, 6:457-481 (1976).

Gorham, E., and W.W. McFee, Effects of Acid Deposition upon Outputs from Terrestrial to Aquatic Ecosystems, Effects of Acid Precipitation on Terrestrial Ecosystems, T.C. Hutchinson and M. Havas, eds., Plenum Press, New York (1980).

Harvey, H.H., Widespread and Diverse Changes in the Biota of North American Lakes and Rivers Coincident with Acidification, Proc. International Conf. on the Ecological Impact of Acid Precipitation, D. Drablos and A. Tollan, eds., SNSF Project, P.O. Box 61, 1432 Ås-NLH, Norway, pp. 93-99 (1980).

Hendry, G.R., et al., Geological and Hydrochemical Sensitivity of the Eastern United States to Acid Precipitation, U.S. Environmental Protection Agency Report EPA-600/3-80-024 (Jan. 1980).

Hendriksen, A., A Simple Approach for Identifying and Measuring Acidification of Freshwater, *Nature*, 278:542-544 (April 1979).

Hendriksen, A., Acidification of Freshwaters - A Large Scale Titration, Proc. International Conf. on the Ecological Impact of Acid Precipitation, D. Drablos and A. Tollan, eds., SNSF Project, 1432 As-NLH, Norway, pp. 68-74 (March 1980).

Holden, A.V., Surface Waters, Ecological Effects of Acid Precipitation, Workshop Proc., Electric Power Research Institute Report EPRI EA-79-6-LD, Palo Alto, Cal. (1979).

Hornbeck, J.W., G.E. Likens, and J.S. Eaton, Seasonal Patterns in Acidity of Precipitation and Their Implications for Forest Stream Ecosystems, *Water, Air, and Soil Pollution*, 7:355-365 (1977).

Impact Assessment Work Group, Aquatic Impact Assessment, Interim Report II, Section 3, U.S.-Canada Memorandum of Intent on Transboundary Air Pollution, U.S./Canada Coordinating Committee, U.S. Department of State, Canadian Department of External Affairs (July 1981b).

Impact Assessment Work Group, Impact Assessment, Interim Report, U.S.-Canada Memorandum of Intent on Transboundary Air Pollution, U.S./Canada Coordinating Committee, U.S. Department of State, Canadian Department of External Affairs (Feb. 1981a).

Johnson, D.W., Site Susceptibility to Leaching by H₂SO₄ in Acid Rainfall, Effects of Acid Precipitation on Terrestrial Ecosystems, T.C. Hutchinson and M. Havas, eds., Plenum Press, New York (1980).

Johnson, N.M., Acid Pain: Neutralization Within the Hubbard Brook Ecosystem and Regional Implications, *Science*, 204:497-499 (May 1979).

Kaplan, E., et al., Rocks, Soils and Water Quality Relationships and Implications for Effects of Acid Precipitation on Surface Water in the Northeastern United States, *Environmental Science and Technology*, 15(5):539-541 (1981).

Kramer, J.R., Geochemical and Lithological Factors in Acid Precipitation, Proc. First International Symp. on Acid Precipitation and the Forest Ecosystem, U.S. Forest Service General Technical Report NE-23, pp. 611-618 (1976).

Last, F.T., et al., Acid Precipitation - Progress and Problems Conference Summary, Proc. International Conf. on the Ecological Impact of Acid Precipitation, D. Drablos and A. Tollan, eds., SNSF Project, P.O. Box 61, 1432 As-NLH, Norway, pp. 10-13 (1980).

Lewis, W.M., Jr., and M.C. Grant, Acid Precipitation in the Western United States, *Science*, 207:176-177 (Jan. 1980).

Likens, G.E., Acid Precipitation, Chemical and Engineering News, pp. 29-44 (Nov. 22, 1976).

Likens, G.E., and T.J. Butler, Recent Acidification of Precipitation in North America, Atmospheric Environment, 15(7):1103-1109 (1981).

Likens, G.E., et al., Acid Rain, Scientific American, 241(4):43-51 (Oct. 1979).

Liljestrand, H.M., and J.J. Morgan, Chemical Composition of Acid Precipitation in Pasadena, California, Environmental Science and Technology, 13(10): 1271-1273 (1979).

McFee, W.W. Sensitivity of Soil Regions to Acid Precipitation, U.S. Environmental Protection Agency Report EPA-600/3-80-013 (Jan. 1980).

Muniz, I.P., and H. Leivestad, Acidification - Effects on Freshwater Fish, Proc. International Conf. on the Ecological Impact of Acid Precipitation, D. Drablos and A. Tollan, eds., SNSF Project, P.O. Box 61, 1432 As-NLH, Norway, pp. 84-92 (1980).

Overrein, L.N., H.M. Seip, and A. Tollan, Acid Precipitation - Effects on Forest and Fish, Final Report of the SNSF Project 1972-1980, P.O. Box 333, Blindern, Oslo, Norway (Dec. 1980).

Schofield, C.L., Processes Limiting Fish Population in Acidified Lakes, Atmospheric Sulfur Deposition: Environmental Impact and Health Effects, D.S. Shriner et al., eds., Ann Arbor Science Publishers, Ann Arbor, Mich. (1980).

Seip, H.M., Acidification of Freshwater - Sources and Mechanisms, Proc. International Conf. on the Ecological Impacts of Acid Precipitation, D. Drablos and A. Tollan, eds., SNSF Project, P.O. Box 61, 1432 As-NLH, Norway, pp. 358-366 (Oct. 1980a).

Seip, H.M., Acid Snow - Snowpack Chemistry and Snowmelt, Effects of Acid Precipitation on Terrestrial Ecosystems, T.C. Hutchinson and M. Havas, eds., Plenum Press, New York (1980b).

Ulrich, B., Production and Consumption of Hydrogen Ions in the Ecosphere, Effects of Acid Precipitation on Terrestrial Ecosystems, T.C. Hutchinson and M. Havas, eds., Plenum Press, New York (1980).

3.5 BIBLIOGRAPHY FOR SECTION 3 - SELECTED BIBLIOGRAPHY ON ACID PRECIPITATION

Almer, B., Effects of Acidification on Swedish Lakes, Ambio, 3(1):30-36 (1974).

Altshuller, A.P., and G.A. McBean, The LRTAP Problem in North America: A Preliminary Overview, prepared by the U.S.-Canada Research Consultation Group on the Long-Range Transport of Air Pollutants, Canadian Embassy, Washington, D.C. (1979).

Aitshuller, A.P., and G.A. McBean, Second Report of the United States Research Consultation Group on the Long-Range Transport of Air Pollutants, Canadian Embassy, Washington, D.C. (Oct. 1980).

Barnes, R.A., The Long-Range Transport of Air Pollution: A Review of European Experience, J. Air Pollution Control Assn., 29(12):1219-1235 (1979).

Beamish, R.J., Acidification of Lakes in Canada by Acid Precipitation and the Resulting Effects on Fishes, Water, Air, and Soil Pollution, 6:501-514 (1976).

Central Electricity Research Laboratories, Ecological Effects of Acid Precipitation, Workshop Proc., Electric Power Research Institute Report EA-79-6-LD, Palo Alto, Calif. (1979).

Drablos, D., and A. Tollan, eds., Proc. International Conf. on the Ecological Impact of Acid Precipitation, SNSF Project, P.O. Box 61, 1432 As-NLH, Norway (Oct. 1980).

GCA Corporation, Acid Rain Information Book, U.S. Department of Energy Report DOE/EP-0018 (1981).

Glass, N.R., G.E. Glass, and P.J. Rennie, Effects of Acid Precipitation, Environmental Science and Technology, 13(11):1350-1355 (1979).

Gorham, E., Acid Precipitation and Its Influence upon Aquatic Ecosystems - An Overview, Water, Air, and Soil Pollution, 6:457-481 (1976).

Grahn, O., H. Hultberg, and L. Landner, Oligotrophication - A Self Accelerating Process in Lakes Subjected to Excessive Supply of Acid Substances, Ambio, 3(2):93-94 (1974).

Hendrey, G.R., and R.F. Wright, Acid Precipitation in Norway: Effects on Aquatic Biota, J. Great Lakes Research, 2(Supplement 1):192-207 (1976).

Hutchinson, T.C., and M. Havas, eds., Effects of Acid Precipitation on Terrestrial Ecosystems, Plenum Press, New York (1980).

Impact Assessment Work Group, Impact Assessment, Interim Report, U.S.-Canada Memorandum of Intent on Transboundary Air Pollution, U.S./Canada Coordinating Committee, U.S. Department of State, Canadian Department of External Affairs (Feb. 1981).

Likens, G.E., Acid Precipitation, Chemical and Engineering News, pp. 29-44 (Nov. 22, 1976).

Likens, G.E., et al., Acid Rain, Scientific American, 241(4):43-51 (1979).

Oden, S., The Acidity Problem - An Outline of Concepts, Water, Air, and Soil Pollution, 6:137-166 (1976).

Overrein, L.N., H.M. Seip, and A. Tollan, Acid Precipitation - Effects on Forest and Fish, Final Report of the SNSF Project 1972-1980, P.O. Box 333, Blindern, Oslo, Norway (Dec. 1980).

Proc. Advisory Workshop to Identify Research Needs on the Formation of Acid Precipitation, D.H. Pack, ed., Electric Power Research Institute Report EA-1074, Palo Alto, Calif. (1979).

Proc. First International Symposium on Acid Precipitation and the Forest Ecosystem, L.S. Dochinger and T.A. Seliga, eds., U.S. Department of Agriculture Forest Service General Technical Report NE-23, Northeastern Forest Experiment Station, Upper Darby, Penn. (1976).

U.S. Environmental Protection Agency, Acid Rain, EPA-600/9-79-036 (1980).

Wright, R.F., et al., Impact of Acid Precipitation on Freshwater Ecosystems in Norway, Water, Air, and Soil Pollution, 6:438-499 (1976).

4 EFFECTS OF RADIONUCLIDES

4.1 BACKGROUND

Radioactive substances are emitted to the atmosphere from various stages of the nuclear fuel cycle and also from coal-fired power plants. These materials are deposited on bodies of water and on land. Following terrestrial deposition, radioactive substances may also be transported to the aquatic environment. The atmospheric route to the aquatic environment is, therefore, a potential pathway for exposure of man and aquatic biota to radionuclides. The following sections review and examine the potential for impacts from such a pathway for the light-water-reactor fuel cycle and for coal-fired power plants.

Radioactivity is measured in units of curies; one curie (Ci) corresponds to 3.7×10^{10} disintegrations per second. Activity, however, is only one factor related to possible environmental impacts, even if one can accurately account for physical transport in the environment. The half-life of the radionuclide, its chemical characteristics (which greatly influence its behavior in the environment), and the nature of its emissions are also important. In addition, an estimate of dose is needed to evaluate impact. Dose is the amount of energy deposited in a given mass of irradiated material. A dose of one rad corresponds to the deposition of 100 ergs of energy per gram of absorbing material. Dose can be modified by multiplying by a quality factor that relates to the amount of energy transferred per distance traveled by radiation (which in turn is related to biological damage). These factors differ for alpha, beta, and gamma emissions. The dose in rads multiplied by the quality factor (and any other modifying factors) gives a dose equivalent in rems (Roentgen equivalent, man). Dose may be due to internal or external exposure. Since different cells respond in different degrees to radiation, the variable biological sensitivity to radiation should be considered. Ideally, one should compute doses for the various types of cells in an organ and then use appropriate factors to determine the dose equivalent for the organ. Average doses and quality factors are typically used, however.

4.2 RADIONUCLIDES FROM THE NUCLEAR FUEL CYCLE

The uranium fuel cycle that supports light-water reactors (LWR) involves a number of stages. They are described in the first section below, which is followed by a description of the emissions from each stage. Finally, radiological effects from atmospheric inputs to the aquatic environment are reviewed and discussed.

4.2.1 Stages in the Nuclear Fuel Cycle

Detailed descriptions of the light-water-reactor fuel cycle can be found in various references [e.g., U.S. Atomic Energy Commission (1974); U.S. Environmental Protection Agency (1973a,b,c), University of Oklahoma (1975)]. The basic steps are briefly described here, with emphasis on atmospheric releases.

Uranium Mining. Uranium (U) is mined by open pit and underground methods. Approximately 90,000 metric tons of ore containing 0.2% uranium oxide (U_3O_8) are needed to fuel a 1000-MWe reactor each year. Mining operations release uranium and its daughters to the atmosphere. Concentrations of airborne radionuclides in unrestricted areas (600 m or more from release point) are expected to be indistinguishable from the natural background (U.S. Atomic Energy Commission, 1974; U.S. Nuclear Regulatory Commission, 1976).

Milling. Uranium mills convert uranium ore (containing about 0.2% U_3O_8) to yellowcake (containing about 80-83% U_3O_8). A 1000-MWe LWR needs about 200 tons of yellowcake per year. Uranium and its daughters [thorium-230 (^{230}Th), radium-226 (^{226}Ra), and radon-222 (^{222}Rn)] are released from the facility to the atmosphere.

Uranium Hexafluoride (UF_6) Production. Yellowcake is converted to UF_6 gas, which is used in uranium enrichment. Two processes are used for UF_6 production: the dry hydrofluor method and wet-solvent extraction. The first process releases more radioactivity, including uranium, to the atmosphere than the second.

Enrichment. The UF_6 gas contains about 0.7% ^{235}U . Before fuel fabrication, the ^{235}U must be enriched to 2-4%, which is presently done by gaseous diffusion. The separation is based on the mass difference between the ^{235}U and ^{238}U isotopes. Small quantities of uranium are released to the atmosphere during enrichment.

Fuel Fabrication. The UF_6 is converted into UO_2 in the fuel fabrication facility. Pellets of UO_2 are formed and then placed in a cladding to form fuel rods. Some uranium is released to the atmosphere.

Light Water Reactor. Heat from the reactor's fuel elements produces steam, which drives a turbine to generate electricity. Two types of LWR are used in the United States: boiling-water reactors (BWR) and pressurized-water reactors (PWR). In a BWR, heat is transferred as steam directly to the turbine. In a PWR, a dual coolant system transfers heat from the primary coolant loop to the second through a heat exchanger. Water in the primary loop is not allowed to boil. Both types of reactors release tritium, radioactive iodine, and noble gases to the atmosphere, but their emission characteristics differ somewhat.

Fuel Reprocessing. Reprocessing facilities recover usable fissionable material from spent fuel. The recovered material can be sent to an enrichment plant and incorporated in feed material for fuel production. No commercial reprocessing plants are now operating in the United States. Relative to other parts of the fuel cycle, reprocessing plants release large portions of the radioactive emissions. Releases to the atmosphere include tritium, krypton, radioactive iodine, fission products, and transuranics.

Radioactive Waste Management. Nuclear wastes must be isolated for long periods to avoid environmental contamination. Releases to the atmosphere from waste storage should be minimal.

4.2.2 Airborne Radioactive Emissions from the LWR Fuel Cycle

To illustrate the nature of emissions from the fuel cycle to the atmosphere, this section presents representative (model) facilities and their emissions. Characterizations are based primarily on the U.S. Atomic Energy Commission's (AEC) 1974 survey of the uranium fuel cycle.

Table 9 lists facilities in the fuel cycle and specifies their sizes. Table 10 tabulates radioactive emissions to the atmosphere from such facilities. The emissions shown do not characterize any individual facilities, but are designed to be representative and to lead to an overall conservative assessment of environmental effects (AEC, 1974). Facilities were not necessarily selected to provide maximum atmospheric emissions. The LWR and mines have emissions as specified by the U.S. Nuclear Regulatory Commission (1976); the other facilities have emissions based on the AEC survey (1974). The LWR has a 1000-MWe capacity, a typical size. Data for mining, milling, and fuel fabrication are taken from representative individual facilities (AEC, 1974). The model for the UF_6 production plant is a composite of the two facilities in operation and the enrichment facility represents the three plants in operation (AEC, 1974). The reprocessing plant is a composite of the three facilities in operation or planned at the time the AEC study was made; no reprocessing plants are in use at present.

Other characterizations of the fuel cycle could be presented; however, the one used illustrates the nature of the emissions involved and illustrates facilities similar in size to those assessed in later subsections.

4.2.3 Aquatic Effects of Airborne Emissions

Environmental effects, including aquatic effects, of the LWR fuel cycle have received a great deal of attention. Typically, however, these impacts are related to releases of liquid effluents from the fuel cycle. The concern surrounding radiological impacts is primarily for man; effects on other organisms have been less well examined. In fact, it is often stated that protecting man from radioactive wastes will usually also protect aquatic organisms and populations (International Atomic Energy Agency, 1976; U.S. Nuclear Regulatory Commission, 1976).

Atmospheric transport of radionuclides to the aquatic environment usually is not addressed quantitatively in radiological assessments of the LWR fuel cycle [e.g., Kay and Rohwer (1975), U.S. EPA (1973 a,b,c)]. Other pathways of exposure are usually considered significantly more important and the atmospheric pathway to water is neglected.

To put atmospheric emissions in some perspective, Table 11 lists the aqueous radioactive effluents from the facilities in the fuel cycle. For UF_6 production, enrichment, and fuel fabrication, the liquid releases of uranium and its daughters are from one to three orders of magnitude larger

Table 9 Description of Model Nuclear Facilities
Used in This Study^a

Facility	Annual Capacity	Number of Model, 1000-MWe LWRs Whose Annual Fuel Requirements Are Served by Each Facility
Uranium mine	480,000 t ore	5.3
Uranium mill	960 t U ₃ O ₈	5.3
UF ₆ production	5,000 t U	27.5
Enrichment	10,500 SWU ^b	90
Fuel fabrication	900 t U	26
Fuel reprocessing	900 t U	26

^aSource: U.S. Atomic Energy Commission (1978).

^bSWU: Separative work units in metric tons. An SWU is a measure of effort to separate a quantity of uranium into enriched and depleted portions in an enrichment plant.

than the releases to the atmosphere. Since most of the atmospheric releases will never reach the aquatic environment, atmospheric emissions will be of negligible importance compared to the direct liquid discharges from these stages of the fuel cycle.

The largest emissions to the atmosphere from the fuel cycle consist of noble gases and tritium. Noble gases are inert and tend to remain in the atmosphere. Consequently, their impact on man and aquatic biota via the atmospheric-aquatic pathway will be less than the relative size of the emissions seems to indicate. Tritium is readily incorporated into the hydrological cycle and certainly will be present in the aquatic environment. However, tritium has beta emissions with low average energy, it moves through the body rapidly, it has a uniform distribution in the body (it does not concentrate in one organ), and it has a bioaccumulation factor of 1.0. Therefore, the dose due to tritium is also much less than might be expected on the basis of its emissions.

The U.S. Atomic Energy Commission (1974) survey indicated that the concentration of airborne radionuclides (primarily radon gas) at uranium mines would be indistinguishable from background concentrations in unrestricted areas (more than 600 m away). One would therefore expect minimal impact on the aquatic environment via atmospheric inputs from mining.

Emissions data show that reactors and reprocessing are the stages of the fuel cycle where atmospheric inputs would most likely have the largest impacts on water quality. On the basis of the considerations outlined above, the other stages should be of relatively less importance, as compared to direct discharges.

Table 10 Annual Airborne Radioactive Emissions (Ci/yr) from Model Nuclear Facilities^a

Radionuclide	Facility ^b			
	1000-t/yr U ₃ O ₈ Mill	1000-MWe Reactors ^c		900-t/yr U Reprocessing Plant
		Boiling Water	Pressurized Water	
³ H (tritium)	-	43	1,100	430,000
¹⁴ C	-	9.5	8	600 ^d
Total noble gases ^b	410	7,300	13,000	9 x 10 ⁶
¹²⁹ I	-	-	-	0.06
¹³¹ I	-	0.3	0.025	0.6
¹³³ I	-	1.1	0.023	-
Fission products	-	-	-	26
²²⁶ Ra	0.1	-	-	-
²³⁰ Th	0.1	-	-	-
U ^b	0.2	-	-	-
Transuranics	-	-	-	0.1

^aSource (except as noted): U.S. Atomic Energy Commission (1974).

^bThe following facilities each emit only one category of radionuclide, and therefore are not included in the table headings: 480,000-t/yr uranium mine - 7,100 Ci/yr of total noble gases (estimated from results in ref. in footnote c; emissions of U and daughters not quantified); 5000-t/yr U UF₆ production plant - 0.004 Ci/yr of U; 10,500-SWU enrichment plant - 0.2 Ci/yr of U; 900-t/yr U fuel fabrication plant - 0.005 Ci/yr of U.

^cSource: U.S. Nuclear Regulatory Commission (1976).

^dSource: Estimated using data given in ref. in footnote c for a 200-t/yr U reprocessing plant.

Blaylock and Witherspoon (1975, 1978) assessed effects of the nuclear fuel cycle on the aquatic environment. In all stages except reprocessing, only liquid effluents were considered. Since reprocessing has no liquid effluent, however, atmospheric inputs were included in the assessment. The facilities Blaylock and Witherspoon used are the same sizes as those given in Table 8, except for the reprocessing plant, which would meet the fuel requirements of 42 1000-MWe reactors instead of 26. They used effluent characteristics somewhat different from those tabulated here. Where possible, their analysis was based on measured concentrations in actual effluents. For reactors, the concentrations used were the highest average annual concentrations found for a number of facilities. Generally, the estimates of effluent characteristics were conservative.

Table 11 Annual Aqueous Radioactive Effluents from Model Nuclear Facilities^a (Ci/yr)

Radionuclide	Facility ^b			
	5000-t/yr U UF ₆ Production Plant	900-t/yr U Fuel Fabrication Plant	1000-MWe Reactors ^c	
			Boiling Water	Pressurized Water
³ H	-	-	43	240
Corrosion, activation, and fission products ^b	-	-	~ 0.3	0.2
²²⁶ Ra	0.09	-	-	-
²³⁰ Th	0.04	-	-	-
²³⁴ Th	-	0.3	-	-
U and daughters ^b	1.21	0.5	-	-

^aSource (except for reactor and reprocessing data): U.S. Atomic Energy Commission (1974).

^bThe following facilities each emit only one or no category of radionuclide, and therefore are not included in the table headings: reprocessing plant - no aqueous emissions^c; 480,000-t/yr uranium mine - U and its daughters may be released, but are not quantified in the refs. in footnotes a and c; 1000-t/yr U₃O₈ mill - 11 Ci/yr of U and daughter products; 10,500-SWU enrichment plant - 1.8 Ci/yr of U and daughters (activation and fission products would be released if recycling were used).

^cSource: U.S. Nuclear Regulatory Commission (1976).

In Blaylock and Witherspoon's 1978 analysis, they assumed that the conservatively estimated liquid discharges were diluted in streams with the arbitrary flow of 1300 ft³/s. Radiation dose to aquatic biota in these streams and to man via the pathways of swimming, drinking water, and eating fish were estimated. Atmospheric emissions from the reprocessing facility were assumed to be deposited on the surface of a stream at some unspecified rate, presumably one typical of conditions 0.8 km from the plant in the direction of prevailing winds. The river segment studied was 1.6 km long by 0.16 km wide and 3 m deep. The analysis actually treated the stream as a lake (no flow) and determined doses for steady-state conditions.

Aquatic organisms may concentrate radionuclides to levels higher than those found in the water column. Therefore, internal dose will provide the major portion of the total dose to such organisms (Blaylock and Witherspoon, 1978). Safe levels of radioactivity for man are generally regarded as not providing dangerous external radiation for aquatic biota. Blaylock and Witherspoon considered only internal doses for aquatic biota.

The effect on biota is a function of the actual radionuclides present, their concentrations, and each species' bioaccumulation factor for a particular radionuclide, and it depends on whether the water is fresh or saline. As an example of the variability of bioaccumulation, consider the factors used by Blaylock and Witherspoon. For $^{232-238}\text{U}$, the factor was 1000 for aquatic plants in freshwater, 67 for plants in saltwater, and 10 for fish in saltwater and freshwater. For $^{131-135}\text{I}$, the factor was 40 for freshwater plants, 10,000 for saltwater plants, 15 for freshwater fish, and 3 for saltwater fish. Generally, for uranium and its daughter products, bioaccumulation factors decrease (and therefore doses decrease also) with increase in trophic level.

On the basis of their analysis, Blaylock and Witherspoon (1978) estimated the maximum doses from the fuel cycle for aquatic plants to be 5 rads/yr (from milling), for invertebrates to be 1.8 rad/yr (from a BWR) and for fish to be 0.14 rad/yr (from a BWR), all for freshwater biota. Other stages provided lower doses. The reprocessing plant provided (via the atmosphere) doses of 0.15, 0.027, and 0.012 rad/yr for freshwater aquatic plants, invertebrates, and fish, respectively. For such low dose rates, Blaylock and Witherspoon indicate, no measurable detrimental effects should occur in the aquatic populations. They indicate that somatic or reproductive effects would be difficult to detect in aquatic populations receiving a dose of 1 rad/d or less. In terms of radiation-induced mutations, Blaylock and Trabalka (1979) state that deleterious effects should not be significant in populations of aquatic organisms for the dose rates above. This conclusion is based on high reproductive rates, strong selective pressures, and a low value of individual organisms to the population.

Studies by the International Atomic Energy Agency (1978) and Blaylock and Trabalka (1978) give detailed reviews of the effects of ionizing radiation on aquatic biota.

To estimate doses to man, Blaylock and Witherspoon (1978) assume that an individual consumes 20 g of fish and 1.2 L of water per day and is exposed 1% of the time from swimming. Their assessment is generally conservative. For example, they assumed all radionuclides that have been measured in the liquid effluent of a commercial reactor were present, although this would not be the case for any individual reactor. Also, they assumed no loss of radionuclides from the water column to sediments. The largest total body dose from swimming, eating fish, and drinking water was from a BWR, for which they estimated a dose of 3.9 mrem/yr. Mining and the BWR contributed doses to bone of 7.1 mrem/yr and 5.1 mrem/yr, respectively. The total body dose for reprocessing (via the atmospheric route to water) was 0.18 mrem/yr, while the reprocessing dose to bone was 0.3 mrem/yr. For comparison, the average annual whole-body dose due to natural radiation in the U.S. is 130 mrem/yr (Klement et al., 1972). Blaylock and Witherspoon indicate that, in most cases, a much larger percentage of potential exposure is due to atmospheric releases than to liquid discharges (contact with atmospheric releases occurs through subsequent inhalation, ingestion of food, and external exposure due to submersion and direct radiation from radionuclides deposited on the ground).

The radiological effects of atmospheric inputs from the LWR fuel cycle to the aquatic environment have not been well quantified. The only analysis this review located was the work of Blaylock and Witherspoon for the fuel-reprocessing stage in the cycle. Atmospheric inputs from that stage to the aquatic environment had no significant effects.

Most atmospheric emissions from the fuel cycle do not reach the aquatic environment, but are deposited on the land surface, where most remain.* Liquid effluents, in contrast, are discharged directly to a body of water. In addition, atmospheric emissions are distributed over a wide area, again in contrast with liquid effluents, which are discharged in a concentrated manner. Therefore, much larger emissions to the atmosphere are required to produce the same level of effect on the aquatic environment as that which results from a given release of liquid effluents.

Since the aqueous discharge of uranium and its daughters is much larger than atmospheric discharge for UF_6 production, enrichment, and fuel fabrication, and since these stages have small radiological impacts from their liquid releases, it seems safe to conclude that atmospheric inputs to bodies of water from these stages will have very small radiological impacts on aquatic biota and man.

Blaylock and Witherspoon (1978) found no significant effect on man or aquatic biota from atmospheric inputs due to reprocessing.

Atmospheric releases from mining are primarily radon gas. This gas is inert and little impact on the aquatic environment is expected. The effects of radon releases have not been quantified, but releases of several orders of magnitude more activity due to krypton from reprocessing apparently have no significant aquatic impact.

Milling releases a smaller quantity of radon gas plus quantities of uranium and its daughters. Atmospheric releases of the latter are roughly an order of magnitude less than aqueous releases from milling. Effects of atmospheric releases from milling should be very small.

Aquatic impacts of atmospheric releases from operation of LWR have not been quantified. Except for iodine-133 (^{133}I), atmospheric emissions from reprocessing are larger than those from either a BWR or a PWR. Although their effects have not been quantified, atmospheric releases from LWR have been neglected in comparison to aqueous releases (which are very small). Therefore, aquatic impacts from LWR atmospheric releases are expected to be small.

It seems reasonable to conclude that aquatic effects (on man and biota) of atmospheric releases from the total LWR fuel cycle should not be of great concern. The major atmospheric impacts in the fuel cycle are from the reactor

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*An exception is lakes that occupy a large fraction of their drainage basin and also occupy a significant fraction of the area of deposition. The Great Lakes might be in this category.

and reprocessing stages. Only the impact of reprocessing has been quantified. Quantification is needed for aquatic impacts of atmospheric releases from all stages of the fuel cycle.

4.3 RADIONUCLIDES FROM COAL-FIRED POWER PLANTS

In addition to the trace elements discussed in Sec. 2, coal also contains trace amounts of naturally occurring radionuclides [^{238}U , ^{232}Th , potassium-40 (^{40}K), and their daughter products]. As with trace elements, releases of radionuclides from coal-fired plants are not regulated. Combustion of coal or its conversion to liquid or gaseous forms concentrates the noncombustible trace constituents, including radionuclides, in the ash or releases them in gaseous form. The more volatile radionuclides (e.g., ^{210}Pb) are also significantly enriched due to their association with small fly-ash particles, which are less efficiently removed by electrostatic precipitators (Coles et al., 1978).

Mean concentrations of natural U, natural Th, and total K in coal of 1.7 $\mu\text{g/g}$, 4.5 $\mu\text{g/g}$, and 1700 $\mu\text{g/g}$, respectively, are reported by Beck et al. (1980) on the basis of many samples from a variety of mines. These concentrations correspond to activities of 0.6 pCi/g, 0.5 pCi/g, and 1.4 pCi/g, respectively. For comparison, Beck et al. (1980) provide average values for concentrations of U, Th, and K in soils of 1.8 $\mu\text{g/g}$, 6 $\mu\text{g/g}$, and 17,000 $\mu\text{g/g}$. As these numbers suggest, the activity in coal is usually less than in soil. However, due to concentration and enrichment, the activity in escaping fly ash can be several times that in typical soil.

A limited number of coal deposits have high concentrations of some radionuclides. These usually occur in low-grade deposits, are mostly in the western United States, and comprise a possible 0.1% of U.S. western coal reserves. On the average, western coals contain smaller quantities of radionuclides (and all trace elements) than other coal (Beck et al., 1980).

As with trace metals, the radionuclides released during coal combustion are the same as those present in the environment. Consequently, detection is difficult since the concentrations of radionuclides in fly ash are not much larger than those in soil. In contrast, radionuclides released from some stages of the nuclear fuel cycle are not naturally present in the environment.

Considering 1000-MWe coal-fired plants with different levels of fly-ash release and different stack heights, Beck et al. (1980) estimated radiation exposures due to radionuclides released to the atmosphere. Average activities in coal were used. The exposure routes they considered were inhalation of air containing fly ash, ingestion of food containing coal-derived radionuclides, and external radiation due to deposited radionuclides. Atmospheric impacts to the aquatic environment were not considered. The most significant pathway was inhalation, and the most critical organ was the lung. Estimated dose equivalents to the lung for maximally exposed individuals are 0.14 mrem/yr for a modern plant releasing 0.1 lb of particulates per 10^6 Btu of fuel and 8.7 mrem/yr for a more poorly controlled plant releasing about 8% of the total ash in the coal, or 0.2-0.5 lb/ 10^6 Btu, depending on the coal's content of ash and heat. These estimates are based on conservative

Table 12 Activities of Emissions from Plants (mCi/yr)

Model for 1000-MWe Coal-Fired Plant	^{238}U decay chain	^{232}Th decay chain	^{40}K	^{222}Rn
Well-controlled modern plant	232	33	31	1000-2000
Poorly controlled plant	1008	312	280	2000-2000

assumptions. For comparison, the two plants release the activities given in Table 12. The estimated average whole-body dose from natural radiation in the United States is 130 mrem/yr (Klement et al., 1972). Beck et al. conclude that: (1) the radiological impact of coal-fired power plants is insignificant; (2) the radiological impact of the coal cycle is much less than that of the uranium fuel cycle when the best available control technology is used; and (3) the radiological impacts of both cycles are very small compared to other sources of radiation.

McBride et al. (1978) also examined the radiological impacts of airborne emissions from a modern 1000-MWe coal-fired plant. They, too, neglected atmospheric inputs to bodies of water. Although the details of their analysis and conclusions differ somewhat from the study by Beck et al. (1980), McBride et al. also concluded that the dose from such plants is much less than that from natural background radioactivity.

On the basis of the assessments described above, it seems reasonable to conclude that the effect on man of radionuclides reaching the aquatic environment via atmospheric emissions from coal-fired power plants is small and probably negligible. Since the more direct pathways of ingestion, inhalation, and direct radiation are of little significance, the much smaller exposure from the pathway involving atmospheric inputs to bodies of water should be of little concern. None of the studies reviewed examined or even mentioned this pathway, or considered the radiological impacts on aquatic biota.

4.4 REFERENCES FOR SECTION 4

Beck, H.L., et al., Perturbations on the Natural Radiation Environment Due to the Utilization of Coal as an Energy Source, Natural Radiation Environment III, T.E. Gesell and W.M. Lowder, eds., Vol. 2, Technical Information Center, U.S. Department of Energy, CONF-780422 (1980).

Blaylock, B.G., and J.R. Trabalka, Evaluating the Effects of Ionizing Radiation on Aquatic Organisms, Advances in Radiation Biology, J.T. Lett and H. Adler, eds., Vol. 7, pp. 103-152, Academic Press, N.Y. (1978).

Blaylock, B.G., and J.P. Witherspoon, Dose Estimation and Prediction of Radiation Effects on Aquatic Biota Resulting from Radioactive Releases from the Nuclear Fuel Cycle, Impacts of Nuclear Releases into the Aquatic Environment, Proc. International Atomic Energy Agency, Vienna, pp. 377-393 (1975).

Blaylock, B.G., and J.P. Witherspoon, Evaluation of Radionuclides Released from the Light Water Reactor Nuclear Fuel Cycle to the Aquatic Environment, Environmental Chemistry and Cycling Processes, D.C. Adriano and I.L. Brisbin, Jr., eds., Technical Information Center, U.S. Department of Energy (1978).

Coles, D.G., R.C. Ragaini, and J.M. Ondov, Behavior of Natural Radionuclides in Western Coal-Fired Power Plants, Environmental Science and Technology, 12(4):442-446 (1978).

International Atomic Energy Agency, Effects of Ionizing Radiation on Aquatic Organisms and Ecosystems, Technical Report Series No. 172, Vienna (1976).

Kaye, S.V., and P.S. Rohwer, Radiological Assessment of Nuclear Power Stations, Advances in Radiation Biology, J.T. Lett and H. Adler, eds., Vol. 5, Academic Press, N.Y. (1975).

Klement, A.W., Jr., et al., Estimates of Ionizing Radiation Doses in the United States 1960-2000, U.S. Environmental Protection Agency Report ORP/CSD 72-1 (1972).

McBride, J.P., et al., Radiological Impact of Airborne Effluents of Coal and Nuclear Plants, Science, 202(8):1045-1050 (1978).

U.S. Atomic Energy Commission, Environmental Survey of the Uranium Fuel Cycle, WASH-1248, Washington, D.C. (1974).

U.S. Environmental Protection Agency, Environmental Analysis of the Uranium Fuel Cycle, Part I -- Fuel Supply, EPA-520/9-73-003-B (1973a).

U.S. Environmental Protection Agency, Environmental Analysis of the Uranium Fuel Cycle, Part II -- Nuclear Power Reactors, EPA-520/9-73-003-C (1973b).

U.S. Environmental Protection Agency, Environmental Analysis of the Uranium Fuel Cycle, Part III -- Nuclear Fuel Reprocessing, EPA-520/9-73-003-D (1973c).

U.S. Nuclear Regulatory Commission, Final Generic Environmental Statement on the Use of Recycle Plutonium in Mixed Oxide Fuel in Light Water Cooled Reactors, NUREG-0002, Vol. 3 (1976).

University of Oklahoma Science and Public Policy Program, Energy Alternatives: A Comparative Analysis, available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. (1975).

5 EFFECTS OF ORGANIC COMPOUNDS

5.1 BACKGROUND

Processes in the energy sector produce a wide variety of organic compounds that may subsequently be released to the atmosphere. A portion of these organics reach the aquatic environment. Although detailed treatment of this complicated subject is beyond the scope of this review, this presentation indicates some pollutants that may be, or are, of concern in the aquatic environment. Indeed, a detailed analysis of most organic emissions is not available, much less an assessment of their aquatic impacts.

Polycyclic aromatic hydrocarbons* (PAH) are considered first below. A few of these compounds have been studied extensively, although the effect on the aquatic environment of atmospheric PAH emissions from the energy sector has not been considered in detail. Some other organics of possible concern are then also discussed briefly.

5.2 POLYCYCLIC AROMATIC HYDROCARBONS

Concern has been expressed over the release of PAH to the environment because some of these compounds are carcinogenic to mammals. The PAH consist of two or more fused aromatic (benzene) rings. Rings are fused when a pair of carbon atoms are shared. These compounds differ in terms of the number and positions of aromatic rings and in terms of the substituents on the rings. Emissions of PAH generally consist of a number of distinct compounds; however, results may not always be presented for individual chemicals. Benzo[a]pyrene (BaP) is often used as an indicator of PAH, since it is strongly carcinogenic, is one of the most ubiquitous of the group, and has been extensively studied. It nevertheless constitutes only a small fraction of all PAH.

5.2.1 Sources of PAH

Combustion processes induced or controlled by man are by far the most quantitatively significant sources of PAH (Suess, 1976). The compounds are also biosynthesized by plants and microorganisms and produced by volcanic activity and by natural fires in forests and grasslands, although quantities of PAH produced by natural sources are relatively small (Suess, 1976).

Table 13 summarizes benzo[a]pyrene emissions to the atmosphere. Emission factors were multiplied by activity levels to give speculative estimates of emissions. Table 13 indicates that stationary sources are considerably larger producers of BaP than vehicles. Improved emission controls should reduce the vehicular contribution even further. Most emissions of BaP are from relatively inefficient combustion, e.g., small furnaces and the burning of coal-mine refuse. For example, to obtain the National Research Council (NRC) results in Table 13, the emission factors used were $1.7 \times 10^6 - 3.3 \times 10^6$ μg of BaP per 10^6 Btu for residential furnaces, 20 - 400 μg of BaP per

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*Also called polynuclear aromatic hydrocarbons.

Table 13 Estimated Benzo[a]pyrene Emissions from
Stationary and Transportation Sources in
the United States

Source	Benzo[a]pyrene Emissions (ton/yr)	
	NRC Estimate ^a	EPA Estimate ^b
Coal		
Residential furnaces	420	270
Intermediate-size furnaces	10	6
Coal-fired power plants	1	<1
Burning coal-mine refuse	340	281
Oil		
Heat and power generation	2	2
Gas		
Heat and power generation	2	2
Wood		
Heat and power generation	40	23 ^c
Incineration		
Enclosed	33	3
Open ^d	214	24
Industry		
Petroleum catalytic cracking	6	6
Coke production	192	0.05 to 153
Vehicles		
Gasoline and diesel fuel	22	10
Rubber tire degradation	-	10

^aSource: National Research Council (1972).

^bSource: U.S. Environmental Protection Agency (1975).

^cHome fireplaces.

^dBurning coal refuse is included under Coal; 140 tons of the 214 shown for NRC are from forest and agricultural burning.

10⁶ Btu for power plants, and 50,000 µg of BaP per 10⁶ Btu for wood burning (NRC, 1972). The EPA (1975) reviewed the NRC (1972) tabulation of BaP emissions and provided estimates of emissions of various types of polycyclic organic matter from different types of residential furnaces, coal-fired power plants, and incineration and open burning. The EPA report says that the emission estimates by NRC are often not well founded. This comment applies particularly to the larger sources in Table 13. However, the only major changes in emissions estimates given by EPA are for the incineration and coke-production categories.

Coal-mining refuse can be ignited spontaneously or by brush or camp fires, and burning has been common in coal-mining areas. However, a recent study (Wahler and Associates, 1978) indicates that burning is largely confined to old deposits, which contain substantial amounts of combustible material and are loosely piled. Modern refuse piles seldom burn because they contain less combustible material and their permeability to air is lower. The emissions from refuse burning and from incineration are order-of-magnitude estimates. The NRC study used a crude estimate of 1.8 g of BaP per ton of coke to obtain results for coke production. The EPA estimates are based on a range of values from different studies.

Table 13 indicates that coal-fired power plants are relatively small sources of BaP. They have highly efficient combustion and efficient emission controls. In spite of these factors, though, they may still be locally significant sources. The PAH emissions from coal-fired power plants may be underestimated by as much as an order of magnitude due to neglect of vapor-phase PAH emissions (Guerin, 1977). Even with an order of magnitude increase, however, such facilities make only a minor contribution to PAH emissions.

Emission estimates for coal-fired power plants are for the conventional type boilers available in the early 1960s. The EPA (1975) said that no test results had been reported for BaP or other polycyclic organic matter from two-stage combustion, which is viewed as a replacement for conventional boilers in order to meet nitrogen-oxide standards.

If the estimated emissions are realistic and have not been greatly reduced as a consequence of modern refuse-pile construction techniques, coal-refuse burning appears to be a major source of PAH that should receive additional study. Increased use of wood stoves may also contribute potentially troublesome amounts of PAH.

5.2.2 Environmental Transport of PAH

Polycyclic aromatic hydrocarbons occur in the atmosphere in particle form (NRC, 1972; Suess, 1976). In or near an exhaust stack, vapors condense on existing particles or form particles themselves. On the basis of a comparison with chlorinated hydrocarbons, Neff (1978) suggests that lower-molecular-weight PAH may also be present in the atmosphere in vapor phase. Atmospheric PAH is removed by both wet and dry deposition.

In the atmosphere, PAH is degraded appreciably by photooxidation, by reaction with oxidants, and by reaction with sulfur oxides (NRC, 1972; Neff, 1979). The most important surface inputs of PAH from the atmosphere, therefore, will probably be located near sources of combustion, with deposition at large distances being limited (Suess, 1976). However, dispersal of particles containing PAH over hundreds or thousands of miles is possible (Neff, 1979). Reactions of PAH during atmospheric transport may produce compounds that are carcinogenic (Neff, 1979).

Estimated quantities of PAH and BaP entering the aquatic environment are significantly less than amounts delivered to the atmosphere or to land (Neff, 1979). The solubilities of PAH in water are low and PAH tends to become adsorbed to particulate matter in the water. Much is delivered to the

sediments. Bioaccumulation occurs, but biomagnification is of limited importance. Photo- and biological oxidation degrade PAH in water. Therefore, PAH in anoxic sediments may remain for long periods, even geological times (Neff, 1979).

5.2.3 Water-Quality Effects of Atmospheric Inputs of PAH

The impact of PAH on aquatic biota may be summarized as follows, based on the account presented by Neff (1979). The PAH are acutely toxic to freshwater and marine animals at concentrations of about 200-10,000 $\mu\text{g/L}$. Concentrations in the range 5-100 $\mu\text{g/L}$ sometimes produce deleterious sublethal effects. The relationship of PAH to carcinogenesis in aquatic biota is unknown.

Since PAH are consent decree pollutants, EPA recently published information on water-quality criteria for the compounds (Federal Register, 1980). Because of a lack of data, no criteria on acute or chronic toxicity were established for freshwater aquatic life. No data were available on chronic toxicity to saltwater aquatic life. The EPA stated that acute toxicity can occur at PAH levels as low as 300 $\mu\text{g/L}$ for saltwater aquatic life. It estimated that a water concentration of PAH of 0.0028 $\mu\text{g/L}$ would result in a 10^{-6} incremental increase of cancer risk over a lifetime due to exposure through ingestion of water and contaminated aquatic organisms. (This corresponds to one case of cancer in an exposed population of one million.) The contribution from drinking water and contaminated organisms is thought to be a minor source of PAH for man (Neff, 1979), since other pathways for exposure provide much larger intakes.

Atmospheric inputs are an important source of PAH to the aquatic environment (Neff, 1979; Suess, 1976). As Table 13 and the accompanying discussion show, PAH released to the atmosphere is predominantly from inefficient sources of combustion. Most of these sources do not belong to what is normally considered the "energy sector." However, coal-refuse burning may make a sizable contribution to atmospheric inputs. If they are considered energy-related sources, home coal and wood burning constitute important inputs from the energy sector.

The following conclusions concerning PAH can be made:

- No quantitative assessment of the aquatic impact of PAH arising from the energy sector is available.
- Coal-refuse burning, particularly of poorly constructed refuse piles, should be examined more carefully as a possibly important source of PAH for the aquatic environment in certain areas.
- Increased use of wood and coal for heating may enhance local PAH levels in the aquatic environment.
- Coal-fired power plants (as well as gas- and oil-fired plants) are a relatively small source of PAH but may affect the local aquatic environment.

5.3 OTHER ORGANIC COMPOUNDS

Various vapor-phase organics can also be released to the atmosphere as a result of activities in the energy sector. These compounds can be quite varied in nature, are often not well studied, and may affect surface-water quality in ways usually not well understood. Energy-related sources do not contribute a majority of the atmospheric emissions of most of these organics.

To put energy-sector emissions into better perspective, consider the estimates of national organic emissions reviewed by the National Research Council (1976). Based on their study, annual emissions of about 30×10^6 ton/yr can be estimated for stationary sources for a period near 1970. The major source (7.1×10^6 ton/yr) is solvent evaporation. Solid-waste combustion, agricultural burning, and forest fires contribute about another 12×10^6 ton/yr. Petroleum-related sources contribute about 4×10^6 ton/yr and fuel combustion adds $4-5 \times 10^6$ ton. For stationary sources, organic acids are the most important constituent of organic emissions, followed by hydrocarbons and aldehydes.

Mobile sources provide a quantity of organic emissions of the same order of magnitude as stationary sources (NRC, 1976), but with an entirely different composition. Natural sources contribute considerably more than man-made ones, but their emissions consist mostly of methane and terpenes, which are not major emissions from anthropogenic sources. Fuel combustion and the handling, storage, and processing of petroleum contribute a significant fraction of total organic emissions. The character of the emission varies with source, fuel, and nature of emission controls.

Atmospheric organics in the vapor phase are removed by wet and dry deposition and some find their way into surface waters. These compounds and their degradation products have the potential for adversely affecting water quality. Adding organics to the aquatic environment also influences the transport of trace metals by increasing their solubility due to complexation. The NRC (1976) study on vapor-phase organic pollutants suggests that their contributions to the effects in natural water just mentioned are probably not decisive. But it also says that not enough information is available to make a judgment. No quantitative evaluation was located during this review that relates aquatic impacts to vapor-phase organic pollutants from the energy sector.

Polychlorinated biphenyls (PCBs) are a group of organic pollutants that are producing water-quality problems and that originated, in part, in the energy sector. These compounds have been used as dielectrics and coolants in transformers and capacitors, as well as having been used in a variety of other products such as heat-transfer fluids, plastics, pesticides, and lubricants. Because of environmental concerns associated with PCBs, production in the United States was stopped in 1979 and disposal and use of materials containing PCBs is now regulated. During the period of PCB production, however, large volumes of these chemicals were generated. Releases of PCBs during use or due to improper disposal have contaminated the aquatic environment. They can volatilize from landfills and do not degrade completely in low-temperature incinerators. Therefore, current and past disposal of PCBs is now releasing these compounds to the atmosphere. Eisenreich et al. (1981) indicate that most PCBs occur in the vapor phase in the atmosphere.

Murphy and Rzeszutho (1977) estimated a precipitation input of PCBs to Lake Michigan of 5000 kg/yr in 1977. They also estimated 1650 kg/yr from streams and waste water and 2500 kg/yr from dry deposition and small aqueous industrial discharges. More recent estimates summarized by Eisenreich et al. (1981) are 6600-8300 kg/yr for atmospheric inputs to Lake Superior, with 1300 kg/yr from tributaries and about 70 kg/yr from municipal and industrial sources. Sinks, primarily sedimentation, were estimated at 1100-1700 kg/yr. Thus, Lake Superior is accumulating PCBs at the rate of 6300-8000 kg/yr in the water column, which corresponds to an increase in water concentration of as much as 0.0005 $\mu\text{g/L/yr}$ if PCBs are assumed to be in a steady state in the lake. Concentrations of PCBs in precipitation are now about 0.02-0.05 $\mu\text{g/L}$ over the Great Lakes basin (Eisenreich et al., 1981). Levels of PCBs in some species of fish in some lakes exceed Food and Drug Administration guidelines (Murphy and Rzeszutho, 1977). Even with a halt in PCB production, these compounds will continue to be a problem in the Great Lakes for sometime.

Concentrations of PCBs that exceed the Food and Drug Administration's tolerance level of 5 mg/kg have also been reported for fish in some areas outside the Great Lakes (National Research Council, 1979). The reference just cited provides a good discussion of environmental contamination by PCBs. Since PCBs are no longer produced in this country, use of PCB-containing products in the energy sector should not increase. However, existing products, such as transformers in electrical distribution systems, should be used and discarded properly to help minimize their contribution of PCBs to the environment.

Other organic contaminants are released from energy-related activities involving combustion* or biomass production, where pesticides are used. This section did not attempt to provide a comprehensive, in-depth review of organics. Thorough assessments relating energy-sector sources of organic contaminants to water-quality impacts are not available.

5.4 REFERENCES FOR SECTION 5

Eisenreich, S.J., B.B. Looney, and J.D. Thornton, Airborne Organic Contaminants in the Great Lakes Ecosystem, Environmental Science and Technology, 15(1):30-38 (1981).

Federal Register, Water-Quality Criteria Documents: Availability, 45(231):79318 (Nov. 28, 1980).

Guerin, M.R., Energy Sources of Polycyclic Aromatic Hydrocarbons, Oak Ridge National Laboratory Report CONF-770130-2 (1977).

Lee, M.L., et al., Dimethyl and Monomethyl Sulfate: Presence in Coal Fly Ash and Airborne Particulate Matter, Science, 207:186-187 (Jan. 1980).

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*E.g., dimethyl and monomethyl sulfate. Dimethyl sulfate is mutagenic and carcinogenic. These compounds have been detected in emissions from coal-fired power plants (Lee et al., 1980).

Murphy, T.J., and C.P. Rzeszuto, Precipitation Inputs of PCBs to Lake Michigan, J. Great Lakes Research, 3(-4):305-312 (1977).

National Research Council, Particulate Polycyclic Organic Matter, Committee on Biologic Effects of Atmospheric Pollutants, National Academy of Sciences, Washington, D.C. (1972).

National Research Council, Polychlorinated Biphenyls, Committee on the Assessment of Polychlorinated Biphenyls in the Environment, National Academy of Sciences, Washington, D.C. (1979).

National Research Council, Vapor-Phase Organic Pollutants: Volatile Hydrocarbons and Oxidation Products, Committee on Medical and Biological Effects of Environmental Pollutants, National Academy of Sciences, Washington, D.C. (1976).

Neff, J.M., Polycyclic Aromatic Hydrocarbons in the Aquatic Environment; Sources, Fates, and Biological Effects, Applied Science Publishers, Ltd., London (1979).

Suess, M.J., The Environmental Load and Cycle of Polycyclic Aromatic Hydrocarbons, The Science of the Total Environment, 6:239-250 (1976).

U.S. Environmental Protection Agency, Scientific and Technical Assessment Report on Particulate Polycyclic Organic Matter (PPOM), EPA-600/6-75-001 (1975).

Wahler, W.A., and Associates, Pollution Control Guidelines for Coal Refuse Piles and Slurry Ponds, U.S. Environmental Protection Agency Report EPA-600/7-78-222 (1978).

6 EFFECTS OF GASEOUS EMISSIONS

6.1 BACKGROUND

Gaseous emissions from energy-related activities were discussed in all of the preceding sections. Some trace metals, radionuclides, and organics are released as gases. Acid precipitation is also related to gaseous emissions of oxides of sulfur and nitrogen. Consequently, this section focuses on the aspects of SO_x and NO_x emissions from the energy sector that are not related to acid rain.

Combustion of coal and oil in stationary sources is the primary origin of SO_x . Coal combustion by utilities is the major stationary source; other SO_x emissions are from industrial processes and a small amount is from transportation. Natural sources contribute little.

Natural processes are the major sources of NO_x . Nitrogen oxides are also emitted in large quantities from transportation sources and utility combustion. Smaller contributions come from industrial fuel combustion and industrial processes.

Because NO_x and SO_2 are toxic to blue-green algae, they may have direct effects on the aquatic environment. The oxidation of NO_x in the atmosphere to form NO_3 provides a potential source of nutrients to the aquatic environment. The following sections discuss these factors.

6.2 ATMOSPHERIC INPUTS OF NUTRIENTS

Atmospheric inputs of nutrients can constitute a significant fraction of the total nutrient budget of some lakes (Brezonik, 1978). Lakes with small ratios of watershed area to lake surface and with little input of agricultural or municipal runoff are most likely to receive a significant portion of their nutrients from the atmosphere. Also, nutrients from the atmosphere are deposited at the surface, where nutrients are in greatest demand. Brezonik summarizes data for a number of lakes, showing that atmospheric contributions (in rainfall) of total nitrogen can exceed 40% of the total nitrogen input to certain lakes. He concludes that nitrogen inputs from the atmosphere can be sufficient to support moderate production in some lakes. The atmosphere also supplies phosphorus, which does not originate in energy-related activities.

Not all nitrogen received by a lake from the atmosphere is in the form of NO_3 , and not all NO_3 originates in the energy sector. Studies of nutrient budgets for lakes generally cannot identify the sources of nutrients deposited from the atmosphere.

Nutrients are important to the phytoplankton in lakes. Although all the elements required by phytoplankton can act, in principle, as limiting nutrients, phytoplankton are phosphorus-limited in most lakes (Schindler, 1977). Nitrogen in the atmosphere can be made available by nitrogen-fixing

algae. Schindler says this biological mechanism can correct nitrogen deficiencies, at least in some cases. He also suggests that only when phosphorus input is increased (e.g., from agricultural or municipal sources) without accompanying increases in nitrogen and carbon will lakes not have a correlation between phosphorus and standing crop of phytoplankton.

Combustion of fossil fuels in the energy sector can increase inputs of nitrogen to lakes. However, on the basis of the above discussion, such increases should not significantly affect water quality unless they are accompanied by increased inputs of phosphorus from other sources.

6.3 TOXICITY OF SO_2 AND NO_x

Wodzinski et al. (1977) reported that blue-green algae are particularly sensitive to bisulfite and nitrite. These compounds are produced in water from SO_2 and NO_x . The photosynthetic activity of the blue-green algae studied was almost completely inhibited by a bisulfite concentration of 0.1 mmol/L, which is approximately equivalent to a dissolved SO_2 concentration in equilibrium with 0.008 ppm SO_2 in the air. The ambient-air-quality standard for SO_2 is 0.03 ppm for the annual average and 0.14 ppm for the 24-hour average.

Blue-green algae are important nitrogen-fixers in some ecosystems. Inhibition of microbial activities such as primary production, nitrogen fixation, or decomposition can have important consequences in an ecosystem. Wodzinski et al. (1977) found that photosynthetic activity of other algae and respiratory activity of bacteria and protozoa were less sensitive to nitrite and bisulfite than was the photosynthesis of blue-green algae.

Photochemical oxidants from precursors released in fossil-fuel combustion have not been shown to produce any direct effect on aquatic organisms (Glass, 1979). The oxidants probably react at the surface of the water, with little penetration of the water column.

6.4 REFERENCES FOR SECTION 6

Brezonik, P.L., Nutrients and Other Biologically Active Substances in Atmospheric Precipitation, J. Great Lakes Research, 2 (Supplement 1):166-186 (1978).

Glass, N.R., Environmental Effects of Increased Coal Utilization: Ecological Effects of Gaseous Emissions from Coal Combustion, Environmental Health Perspectives, 33:249-272 (1979).

Schindler, D.W., Evolution of Phosphorus Limitation in Lakes, Science, 195:260-262 (1977).

Wodzinski, R.S., D.P. Labeda, and M. Alexander, Toxicity of SO_2 and NO_x : Selective Inhibition of Blue-Green Algae by Bisulfite and Nitrite, J. Air Pollution Control Assn., 27(9):891-893 (1977).

7 CONCLUSIONS

This report has examined the potential for adverse effects on surface freshwater quality due to atmospheric pollutants released from the energy sector. An effort was made to present information in a consistent manner for each class of pollutants considered; differences in presentation reflect in part the differences in the current state of knowledge in different areas. This report was organized by general category of pollutant -- trace elements, organics, etc. Such organization focuses minimum attention on the fact that, in general, all types of pollutants will be delivered to the aquatic environment together. This is because some pollutants are transported over long distances, allowing inputs from a variety of sources to be combined, and also because the combustion of fossil fuels produces emissions containing pollutants in most, if not all, groups considered. Pollutants in a complex mixture are likely to interact in terms of effects they produce on biota. The potential effects on aquatic biota and human health from individual chemicals are often not clearly understood; the possible synergistic and antagonistic effects from combinations of pollutants are even more poorly appreciated. It is primarily because of a lack of knowledge of how pollutants interact that this report has generally treated each category of pollutant in isolation from the others. Based on the material presented, a number of conclusions can be made. These fall into two categories: general conclusions and those related to a specific class of pollutants.

The general conclusions are:

- Energy-related activities can release substantial amounts of pollutants to the atmosphere. These may eventually reach the aquatic environment. The nature of the pollutants varies and potential effects are generally not well quantified.
- Aquatic impacts due to atmospheric inputs of pollutants (some of which are energy-related) or the potential for such impacts can occur in many different areas in the United States. For example, the effects of acid precipitation are most apparent in the Northeast; trace elements and organics are of concern in the Great Lakes; and trace elements also pose a problem in the Northeast, where they may be better mobilized by acidified water, and in the West because of acid conditions. Atmospheric inputs of pollutants to surface water is a national issue.
- Information presently available suggests that acid precipitation produces significant and widespread adverse aquatic effects. Comparable aquatic effects due to other atmospheric inputs from energy-related sources have not been observed. Most other effects are expected to be more subtle.
- Coal combustion is particularly noteworthy because it is a source of all classes of pollutants considered, as well as being the major contributor in some cases.

- For some pollutants, adequate information and methods are available to make assessments of potential effects from deployment of some energy-related technologies. Such assessments may be partially qualitative. For other pollutants (and combinations), fundamental gaps in quantitative understanding still limit the ability to make complete assessments (e.g., quantitatively relating SO_x emissions to H^+ deposition).

Specific conclusions are:

- Acute aquatic effects involving deposition of trace elements from energy-related activities are unlikely, but some chronic effects may occur, in Lake Michigan, for example, where a portion of the trace-element deposition results from energy production. Other areas may be affected by mercury and cadmium emissions from coal-fired power plants. The order-of-magnitude analysis in this report should be refined to account for other conditions than worst-case.
- Atmospheric releases of certain trace elements (for example, mercury) from coal-fired power plants are not well controlled by present technology. More widespread use of electrostatic precipitators will not eliminate the potential problems associated with the release of these elements.
- Acid precipitation cannot be quantitatively related to its sources. Therefore, aquatic impacts that may arise from energy developments cannot be quantified at present. How a watershed responds to acid precipitation is also not fully understood. However, some techniques are available to help assess the sensitivity of areas to acid inputs.
- Researchers have not quantitatively assessed aquatic and human effects of radionuclides that reach bodies of water from the atmosphere and originate in the energy sector. A more qualitative approach suggests that the impacts should not be significant.
- A variety of organic compounds are released from combustion and from other energy-sector activities. Some of these compounds are quite toxic and are known to reach the aquatic environment. Poorly controlled combustion is a major source of some contaminants. No quantitative evaluations are available.
- Oxides of sulfur and nitrogen inhibit photosynthesis in blue-green algae; therefore, direct aquatic impacts of energy-sector air pollutants are possible.

The following topics should be pursued to improve the understanding of water-quality impacts of energy-related atmospheric pollutants:

- Perform additional long-term studies (both theoretical and experimental) of the behavior and effects of trace elements in a number of selected watersheds; improve the ability to estimate atmospheric pollutant deposition.

- Conduct an improved assessment of the potential for water-quality effects of trace-element emissions, including wet deposition explicitly and accounting for the presence of Hg in the atmosphere as a gas.
- Establish a quantitative relationship between power-plant emissions and acid precipitation and explore more fully the related aquatic effects, including those in streams, lakes, and ground water.
- Quantify the aquatic effects of atmospheric deposition of radionuclides from the LWR fuel cycle.
- Define more carefully the nature of organic emissions from the energy sector and assess the potential for aquatic effects.
- Assess the potential for direct effects of air pollutants on blue-green algae.
- Explore the potential for synergistic and antagonistic effects in the aquatic environment from simultaneous inputs of different atmospheric pollutants.

APPENDIX: ANALYSIS OF THE EFFECTS OF ATMOSPHERIC DEPOSITION OF POLLUTANTS ON SURFACE-WATER QUALITY

INTRODUCTION

An assessment is presented in Sec. 2 of the potential effects on water quality of inputs of trace elements via the atmosphere. This appendix presents in detail the basis for the results presented there. First, a description of the atmospheric emissions used in the analysis is given. This is followed by a discussion of the approach used to estimate deposition rates. Next, several simple models used to estimate concentrations of contaminants in surface waters are presented. Finally, a summary of relevant quality criteria for surface water is provided, since such criteria serve as the basis for assessing the severity of potential effects on surface-water quality.

ATMOSPHERIC EMISSIONS

As was noted in Sec. 2, the trace-element composition of coal is quite variable. No attempt was made to account for all such variability in the analysis. For this assessment, one eastern and one western coal type were selected from the group considered by Dvorak et al. (1977). The atmospheric emission rates for plants using these two types of coal were taken from Dvorak et al. and are given in Table A.1.

The two model plants considered have electrostatic precipitators with a 99.5% removal efficiency. For the coals considered, this results in particulate emissions somewhat less than required by revised new source performance standards. The facilities are therefore well controlled. Trace-element emissions are not regulated and must be related to emission of particulates when conducting an assessment of potential impacts.

ATMOSPHERIC TRANSPORT AND DEPOSITION

There is considerable variability not only in the trace-element composition of coal, but in the manner in which emissions from a coal-fired power plant are dispersed following discharge from the plant's stack. Dvorak et al. (1977) analyzed meteorological dispersion of power-plant emissions for a number of locations. Their analysis is based on a modified Gaussian plume model.

Representative meteorological conditions were used for each region studied, and average long-term pollutant concentrations were determined. The plants considered had 300-m stacks. Except rather close to the source, the results should not be very sensitive to the stack height used (Argonne National Laboratory, 1977).

Dvorak et al. presented isopleths of predicted mean annual concentrations of particulates within 50 km of the sites considered. Two of their sites were selected for this study. One is an eastern interior site; the other is located at Four Corners in the Southwest. Using the concentration data from Dvorak et al., and assuming a 0.3-cm/sec deposition velocity,

Table A.1 Atmospheric Emission Rates from Model Plants^a

Element	Eastern Interior, Illinois Coal		Four Corners, Wepo Coal	
	Rate (kg/1000 MWh)	Rate ^b (kg/yr)	Rate (kg/1000 MWh)	Rate ^b (kg/yr)
As	0.03	200	0.01	70
Ba	0.1	600	0.08	500
Cd	0.03	200	0.005	30
Co	0.03	200	-	-
Cr	0.1	600	0.04	200
Hg	0.05	300	0.01	80
Mn	0.1	800	0.02	100
Pb	0.4	2,000	0.05	300
Se	0.09	600	0.09	600
V	0.1	700	0.03	200
Zn	0.8	5,000	0.06	300
PM ^c	70.0	400,000	70.0	400,000

^aBased on model plants considered by Dvorak et al. (1977). Pulverized coal burners are assumed. Plants are 1000 MWe with 99.5%-efficient electrostatic precipitators. All results are rounded to one significant figure.

^bBased on a capacity factor of 70%.

^cParticulate matter.

Source: Adapted from Dvorak et al. (1977).

deposition rates were calculated for model plants at the two locations. The results are presented in Table A.2.

To provide a range of deposition rates, several cases were considered. First, the maximum concentrations given in the results of Dvorak et al. were used to develop a "maximum" deposition rate. Of course, this is not a true maximum, since the plots from which the maximum concentration were taken have limited spatial resolution. However, it does represent the highest concentration over a significant area on a display that has a grid size of about 10 km. In addition, a typical concentration at 50 km downwind of the plant was used to develop a "typical" deposition rate. Also, deposition rates were determined on two assumptions: that deposition is uniform within a radius of 50 km, and uniform within 100 km of the source. Comparison of these last estimates with the maximum and typical deposition rates indicates that trace elements are deposited at locations quite far removed from their sources.

Table A.2 Deposition Rates from Model Plants^a ($\mu\text{g}/\text{m}^2\text{-yr}$)

Element	Eastern Interior, Illinois Coal				Four Corners, Wepo Coal			
	Maximum ^b	Typical ^c	50 km ^d	100 km ^d	Maximum ^b	Typical ^c	50 km ^d	100 km ^d
As	0.87	0.60	26.0	6.5	1.1	0.78	8.5	2.1
Ba	2.6	1.8	77.0	19.0	7.7	5.5	62.0	16.0
Cd	0.68	0.47	21.0	5.0	0.48	0.34	3.8	0.95
Co	0.84	0.57	25.0	6.0	-	-	-	-
Cr	2.8	1.9	83.0	21.0	3.5	2.5	28.0	7.0
Hg	1.3	0.89	38.0	9.5	1.3	0.92	11.0	2.8
Mn	3.4	2.3	100.0	25.0	1.7	1.2	13.0	3.3
Pb	10.0	6.8	300.0	75.0	4.4	3.1	35.0	8.8
Se	2.4	1.6	71.0	18.0	8.8	6.3	71.0	18.0
V	3.0	2.1	88.0	22.0	3.0	2.1	24.0	6.0
Zn	22.0	15.0	650.0	160.0	5.5	3.9	44.0	11.0
TSP	1900	1300	56,000	14,000	6600	4700	53,000	13,000

^aBased on model plants considered by Dvorak et al. (1977). Plants have pulverized-coal burners, are 1000 MWe with 99.5%-efficient electrostatic precipitators, and have a capacity factor of 70%. A particle deposition velocity of 0.3 cm/sec is assumed.

^bBased on isopleth with the maximum particulate concentration displayed by Dvorak et al. (1977).

^cBased on typical particulate concentration at 50 km downwind from plant as shown by Dvorak et al. (1977).

^dBased on assumption that all emissions are deposited uniformly within the radius indicated.

The deposition rates for the trace elements given in Table A.2 are based on the assumption that the ratio of trace-element deposition to the total particulate deposition is the same as the ratio of trace-element emissions to total particulate emissions, as given in Table A.1 (i.e., it is assumed that the trace elements are all associated with particulates). The deposition rates given in Table A.2 were developed to provide a range of values of deposition that might be expected within some tens of kilometers of a source. Actual deposition would be expected to exhibit substantial spatial variability, as suggested by the plots of atmospheric concentrations of particulates given by Dvorak et al.

WATER-QUALITY ANALYSIS

As already indicated, the trace-element composition of coal and the meteorological dispersion of stack emissions can be quite variable. In addition, given the variability in the environment, one would expect appreciably different effects on water quality in different locations. The purpose of this section is to describe several simple models that can be used to estimate changes in concentrations of contaminants in lakes and streams resulting from inputs from the atmosphere.

Lakes

Lakes receive inputs of materials from tributaries, the atmosphere, erosion of shorelines, and from resuspension of sediments, as well as directly from anthropogenic sources. Lakes lose materials through outflows, sedimentation, and also through losses to the atmosphere. This analysis will assume a well-mixed lake (i.e., the concentration of a contaminant is assumed to be uniform throughout the lake). It will neglect inputs from shoreline erosion and point sources and losses to the atmosphere. The analysis assumes that all material delivered to the lake remains in the water column. Since the interest here is in the changes in concentration resulting from atmospheric inputs, it is assumed that these inputs are added to a system that is in equilibrium. Therefore, the most important assumptions mentioned above are those that neglect losses to the atmosphere or to sediments. Since such neglect tends to produce overestimates of concentrations, they are conservative assumptions. The assumption of uniform concentration is probably reasonable, given the long time scales to be considered (e.g., decades), except possibly for very large lakes.

Using a mass balance of a pollutant in a lake, the change in the amount of pollutant during a given period may be calculated as the mass of pollutant added to the lake during the period minus the amount removed during the period. These masses are determined by the relevant deposition rates and the inflow and outflow rates multiplied by the time period.

Thus, if V is the volume of the lake and C is the concentration of the pollutant in the lake, the change in pollutant mass is $V\Delta C$:

$$V\Delta C = \phi(A_w + \alpha A_L) \Delta t + q_i C_{in} \Delta t - q_o C \Delta t \quad (1)$$

where:

ϕ = the atmospheric flux (mass deposited per unit area per unit time) of pollutant being considered,

A_w = the surface area of lake,

A_L = the surface area of terrestrial portion of watershed,

α = the fraction of pollutant deposited on terrestrial surface that reaches the lake,

ΔC = the concentration change in interval Δt ,

q_i = the flow into lake (volume per unit time),

q_o = the flow out of lake (volume per unit time), and

C_{in} = the concentration of the pollutant in the flow into the lake.

In the limit as Δt goes to zero,

$$V \frac{dC}{dt} = \phi(A_w + \alpha A_L) + q_i C_{in} - q_o C \quad (2)$$

Case 1: No outlet. Consider the case of a lake with no outlet, i.e., a closed basin, for which $q_o = 0$.

Solving Eq. 2 gives:

$$C = \frac{\phi}{V} (A_w + \alpha A_L)t + C_o + (q_i C_{in}/V)t \quad (3)$$

where:

C_o = concentration in lake at $t = 0$.

The volume of the lake, V , equals dA_w , where d is the mean depth of the lake. Let $\gamma = A_L/A_w$, the ratio of watershed land area to water area. Then

$$C = \frac{\phi}{d} (1 + \alpha \gamma)t + C_o + (q_i C_{in}/V)t \quad (4)$$

Therefore, in the simple case of a closed lake, the concentration at some future time depends upon the present concentration, to which are added trends due to atmospheric and tributary inputs.

Case 2: Lake with an outlet. In the more general case where there is an outflow, and assuming $C = C_{in}$ at $t = 0$, the solution of Eq. 2 is:

$$C = \frac{\phi}{q_o} (A_w + \alpha A_L) [1 - \exp(-q_o t/V)] + C_{in} \quad (5)$$

For $t \gg V/q_0$, so that the concentration of pollutant in the lake has equilibrated with the pollutant inputs,

$$C = C_{in} + \frac{\phi}{q_0} (A_w + \alpha A_L) \quad (6)$$

The flow from the lake can be written as a function of the annual precipitation, P (depth/yr).

$$q_0 = P(A_L g + A_w) - EA_w$$

where:

g = the fraction of precipitation that reaches the lake from the land surface, and

E = the annual evaporation from lake (depth/yr).

Substituting in Eq. 6 and simplifying yields

$$C = C_{in} + \phi(1 + \alpha\gamma)/[P(\gamma g + 1) - E] \quad (7)$$

Implicit in this derivation is the assumption that $q_0 > 0$, or that $P(\gamma g + 1) - E > 0$.

Streams

Lakes provide a reservoir in which contaminants can accumulate, with their concentrations increasing indefinitely in the case of the simple well-mixed closed basin or approaching an equilibrium value in the case of a basin with some outflow. Streams can be considered as lakes with an outflow but with a very small hydraulic residence time, V/q_0 . In streams, the water is not an important reservoir for long-term accumulation of pollutants, although the sediments may be.

During dry weather, Eq. 5 can be applied to the case of a stream. For such an application, $\alpha = 0$ and $V/q_0 \ll 1$. Then,

$$C = A_w \phi / q_0 + C_{in} \quad (8)$$

where A_w is now the surface area of the stream above the point of interest and the contaminant in the stream is assumed to be conserved. Any resuspension of sediment is neglected, which is likely a good assumption during dry weather.

During wet weather (including periods of snowmelt), the conditions are quite different. The lake model as given in Eq. 5 does not apply, even with $V/q_0 \ll 1$. That model is intended to deal with long-term average conditions; individual events are not considered. However, during wet weather, short-term inputs to a stream tend to provide the principal inputs of material. Pollutants that are deposited on the terrestrial portion of the watershed during dry weather are partially transported to the stream in runoff during wet weather, in addition to pollution delivered to the watershed with the precipitation.

The problem of determining the concentration in runoff is a difficult one, and no solution will be attempted here. Instead, the concentration increase will be estimated using the ratio ϕ/R , where R is the annual runoff (m/yr). Such a calculation assumes that all the material deposited in the basin during a year is diluted in the annual runoff from the basin. As was discussed in Sec. 2, watersheds tend to retain large fractions of trace elements in their soils; therefore the actual mass of trace element available for transport would tend to be much less than ϕ . It is possible, however, that a concentration change greater than ϕ/R could occur during some event. For example, during snowmelt, a large fraction of deposited material might be transported over frozen ground in a relatively small volume of runoff. The ratio ϕ/R is not meant to be a rigorous upper limit on possible concentration changes in runoff. However, it should be reasonably conservative since it overestimates the mass available for transport in runoff by one to two orders of magnitude or more, depending on the trace element being considered.

To obtain an estimate of total concentration, ϕ/R can be added to the background concentration, which exists in the absence of atmospheric inputs.

Summary

Several simplified situations have been considered and expressions have been developed that allow representative surface-water concentrations to be estimated for pollutants that are deposited from the atmosphere. The expressions developed are not intended to provide accurate answers. Their purpose is to provide a means for assessing the possible range of impacts in several general types of situations, and to illustrate explicitly some of the important factors involved in the assessment.

WATER-QUALITY CRITERIA

The assessment of the significance of estimated concentrations of contaminants is based on a comparison with water-quality criteria. The criteria used are summarized in Tables A.3 and A.4. They are based on results presented in the U.S. Environmental Protection Agency's Quality Criteria for Water (1976) and on recently published results for the priority pollutants.

Table A.3 Water-Quality Criteria for Domestic Water Supply and Human Health

Element	Criteria for Domestic Water Supply ^a (µg/L)	Ambient Criteria for Human Health ^b (µg/L)
As	50	c
Ba	1000	-
Cd	10	10
Co	Not specified	Not specified
Cr	50	{ 170 trivalent 50 hexavalent
Cu	1000	Not specified due to lack of data
Hg	2	0.144
Mn	50 (welfare)	-
Ni	Not specified	13.4
Pb	50	50
Se	10	10
V	Not specified	Not specified
Zn	5000 (welfare)	Not specified due to lack of data

^aSource: U.S. Environmental Protection Agency (1976).

^bFor protection of human health from ingestion of water and contaminated aquatic organisms. Source: Water Quality Criteria (Nov. 28, 1980).

^cFor maximum protection of human health, concentration should be zero on the basis of a nonthreshold assumption for this chemical.

Table A.4 Water-Quality Criteria for Freshwater Aquatic Life

Element	Criteria Not To Be Exceeded At Any Time ($\mu\text{g/L}$)	24-hr Average ^a ($\mu\text{g/L}$)
As	440 ^b	not specified
Ba	>50 mg/L before toxicity is expected ^c	>50 mg/L before toxicity is expected
Cd	$\exp [1.05 \ln (\text{hardness}) - 3.73]$	$\exp [1.05 \ln (\text{hardness}) - 8.53]$
Co	not specified	not specified
Cr	$\left\{ \begin{array}{l} 21 \text{ hexavalent} \\ \exp [1.08 \ln (\text{hardness}) + 3.48] \\ \text{trivalent} \end{array} \right.$	0.29 hexavalent not specified for trivalent
Cu	$\exp [0.94 \ln (\text{hardness}) - 1.23]$	5.6
Hg	0.0017	0.00057
Mn	not considered a problem ^c	not considered a problem ^c
N	$\exp [0.76 \ln (\text{hardness}) + 4.02]$	$\exp [0.76 \ln (\text{hardness}) + 1.06]$
Pb	$\exp [1.22 \ln (\text{hardness}) - 0.47]$	$\exp [2.35 \ln (\text{hardness}) - 9.48]$
Se	260	35
V	not specified	not specified
Zn	$\exp [0.83 \ln (\text{hardness}) + 1.95]$	47

^aSource: Water Quality Criteria (Nov. 28, 1980). Hardness is in mg/L as CaCO_3 . All concentrations are total recoverable.

^bFor total recoverable, trivalent, inorganic arsenic.

^cSource: U.S. Environmental Protection Agency (1976).

REFERENCES FOR APPENDIX

Argonne National Laboratory, National Coal Utilization Assessment, An Integrated Assessment of Increased Coal Use in the Midwest - Impacts and Constraints, Volume II, ANL/AA-11 (Oct. 1977).

Dvorak, A.J., et al., The Environmental Effects of Using Coal for Generating Electricity, U.S. Nuclear Regulatory Commission Report NUREG-0252 (1977)

Water Quality Criteria, Federal Register, 45:79318 (Nov. 28, 1980).

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