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ATMOSPHERIC SCIENCES PROGRAM

Summaries of Research in FY 1993

U.S. Department of Energy
Office of Energy Research
Office of Health and Environmental Research
Environmental Sciences Division
Washington, D.C. 20585

MASTER *rb*

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FOREWORD

Fiscal year 1993 has been an exciting time for the Atmospheric Sciences Program. We launched a new research effort to address upper-tropospheric and lower-tropospheric ozone in the midlatitudes. The first awards in this program are reported in this publication. The research is managed within our Atmospheric Chemistry Program (ACP). This research will be closely coordinated with the U.S. Global Change Research Program (USGCRP), and in FY 1995, the research will be reported as part of the Nation's focused global change research. The reader is advised to peruse the DOE publication, *Global Change Research: Summaries of Research in FY 1993* (DOE/-0597T), which includes many atmospheric-science research efforts in climate change.

In pursuing atmospheric research, we will continue to focus on activities that respond to the DOE mission, national needs, and international opportunities. In particular, we will be developing research priorities to address the National Energy Policy Act of 1992. As the reader will quickly see, the ACP products are directly aimed at these stakeholders.

The Atmospheric Dynamics Program continues its tight focus on the planetary boundary layer in complex terrain. Research at the DOE Rocky Flats facility has the double benefit of producing data for a DOE site-specific application as well as contributing to general scientific understanding of the planetary boundary layer. As the USGCRP begins to explore Earth-system models, such information will be essential to link the surface processes to the free atmosphere.

I would like to take this opportunity to thank Mike Riches, Program Manager for Atmospheric Sciences; Jake Hales, Science Director of the ACP; and Chris Doran, Scientific Director for Atmospheric Dynamics, for their inspired leadership and sustained commitment to all stakeholders. I would also like to thank F. M. O'Hara, Jr., for his continued assistance in this document's compilation and publication.

Ari Patrinos, Director
Environmental Sciences Division
Office of Health and Environmental Research
Office of Energy Research

PREFACE

This document describes the activities and products of the Atmospheric Science Program of the Environmental Sciences Division, Office of Health and Environmental Research, Office of Energy Research, in FY 1993. The report is organized into four main sections.

SECTION	DESCRIPTION
Introduction	▶ Provides a mission statement, need, and mandate for an atmospheric science program ▶ Ties atmospheric science issues to the research approach, program goals, and objectives ▶ Relates each specific research area to the overall goals of the program ▶ Shows the level of effort
Research Areas and Project Descriptions	▶ Describe scientific questions in each research area ▶ Provide descriptions of individual research projects ▶ List the expected product for each project ▶ Show the research approach or methodology used in each project ▶ Provide results to date when applicable
Appendixes	▶ Provide addresses of principal investigators and define acronyms used in the text
Indexes	▶ Provide locator information on subjects, principal investigators, and research institutions for the overall report

Questions concerning the Atmospheric Science Program or specific projects may be addressed to the Environmental Sciences Division, U.S. Department of Energy, ER-74, Washington, DC, 20585. The Program's telephone number is (301) 903-3281.

INTRODUCTION

MISSION AND MISSION NEED

Meeting the nation's energy needs imposes anthropogenic demands on the environment. A basic understanding of how the atmosphere and the terrestrial and marine ecosystems transport, transform, and cycle energy-related materials and how these systems respond to natural and human-induced changes is required to ensure that future energy sources can be secured and that environmental quality is protected and enhanced.

The mission of the Department of Energy's (DOE's) Environmental Processes and Effects Research (EPER) Program, in which the Atmospheric Science Program resides, is to (1) quantify the physical, chemical, geological, and biological processes that transport, disperse, and transform energy-related materials in the atmosphere and in terrestrial and marine ecosystems; (2) to determine the mechanisms of degradation and detoxification of hazardous energy-related materials in the environment; and (3) to determine and manage the capacity for ecosystem adjustments to energy-related environmental stresses.

The EPER Program primarily addresses the environmental components of the National Energy Policy Act of 1992 (EPACT) that are local to regional in character (e.g., environmental restoration at contaminated DOE facilities and atmospheric modeling for emergency response). The program also complements the Office of Health and Environmental Research (OHER) Global Change Program addressed elsewhere. Research within the EPER Program provides scientific data as well as modeling, geochemical tracer, and biotechnological tools. These tools are needed to link the physical, chemical, and biological processes operating at molecular scales with the

atmosphere-marine-terrestrial feedback mechanisms that operate at regional and global scales. Research on tropospheric and stratospheric ozone is also included. Small Business Innovative Research (SBIR) activities focus on developing advanced measurement technologies needed for environmental research.

PROGRAM MANDATES

Mandates to conduct research on environmental processes and effects include the Atomic Energy Act of 1954 (PL 83-703), authorizing the conduct and support of research and development related to the preservation and enhancement of a viable environment; the Energy Reorganization Act of 1974 (PL 93-438), promoting environmental research related to the development of energy sources and utilization technologies; the Federal Nonnuclear Energy Research and Development Act of 1974 (PL 93-557), authorizing a comprehensive nonnuclear energy research, development, and demonstration program including environmental consequences of energy technologies; and the Department of Energy Organization Act of 1977 (PL 95-91), mandating the Department to "assure incorporation of national environmental protection goals in the formulation and implementation of energy programs and to advance the goal of restoring, protecting, and enhancing environmental quality and assuring public health and safety" and to conduct "a comprehensive program of research and development on the environmental effects of energy technology."

Research on environmental processes and effects also supports mandates in EPACT (PL 102-486), which calls for DOE to evaluate the environmental benefits and costs of technologies to improve energy efficiency and of technologies and

processes for preventing pollution. EPACT also mandates DOE to evaluate and compare the environmental performance of clean coal technologies relative to that of other conventional technologies.

PROGRAM RELATIONSHIPS

At the interagency level, EPER Program components are coordinated via the subcommittees and working groups of the Committee on Earth and Environmental Sciences (CEES) of the Federal Coordination Council for Science, Engineering, and Technology (FCCSET). For example, the Subsurface Science Program interacts with the Subcommittee on Water Resources; the Ocean Margins Program contributes to both the Working Group on Global Change (WGGC) and the Working Group on Coastal Ocean Science; and the Atmospheric Sciences Program is a major participant in the Subcommittee on Atmospheric Research and the WGGC.

In addition to the FCCSET process, EPER programs pursue other intra-agency and interagency collaborations. The Subsurface Science Program coordinates with DOE's Office of Environmental Restoration and Waste Management and other agencies (e.g., the Nuclear Regulatory Commission and the U.S. Geological Survey) by joint research funding and cooperative field studies; this program also sponsors research in collaboration with industry, such as oil companies, and has a formal technology-transfer program that moves basic research results to DOE sites and industry. The Ocean Margins Program has joined forces with the National Science Foundation (NSF) in the Joint Global Ocean Flux Study. The Environmental Radon Program is a part of OHER's Radon Research Program, which coordinates with DOE's Office of Conservation and Renewable Energy and the U.S. Environmental Protection Agency via a memorandum of understanding (MOU).

PROGRAM OBJECTIVES

The objectives of EPER are to develop the scientific tools to assess the environmental conse-

quences of energy-related activities and to promote improvements in environmental quality. EPER currently includes five distinct components that address different problem areas of high priority to DOE:

- I. The **Subsurface Science Program** emphasizes long-term mechanistic research within the subsurface biosphere; it contributes to resolving problems of contaminant transport that result from surface and shallow land burial of defense and energy-related wastes and to environmental restoration at DOE sites.
- II. The **Environmental Radon Program** encompasses basic research on the sources and transport of radon in the environment and on processes that can affect its entry into buildings.
- III. The **Ocean Margins Program** addresses a quantitative understanding of the dispersal and fate of energy-related materials at the land/ocean interface. The principal focus of this program is on the fluxes of carbon in the coastal ocean and their implications to the global carbon cycle and, therefore, to global climate change.
- IV. The **Program for Ecosystem Research** examines the processes of ecosystem adjustment to environmental changes and uses this understanding to protect and restore ecosystems that are adversely impacted or threatened by energy production and use.
- V. The **Atmospheric Sciences Program** develops a comprehensive understanding of the atmospheric processes that control the transport, transformation, and fate of energy-related air pollutants. The objectives are (1) to understand the atmospheric-chemistry processes of energy-related air pollutants (e.g., sulfur and nitrogen oxides and ozone) in both gas and aqueous phases and their gas-to-particle conversion and fate, including deposition and resuspension; (2) to understand the meteorological processes that control the

dispersion of material releases to the atmosphere over complex terrain (e.g., in mountainous regions); (3) to develop predictive models for the above processes and to acquire the data to validate them; and (4) to develop an understanding of the trends in mid-altitude stratospheric ozone change and the heterogeneous chemistry and dynamics controlling ozone in this region.

ATMOSPHERIC SCIENCE PROGRAM STRATEGY

The Atmospheric Science Program involves interdisciplinary field and laboratory research and modeling activities. Where appropriate, research is conducted at DOE sites. Research focuses on developing a mechanistic understanding of the processes controlling the environmental transport, transformations, and fate of energy-related materials in the atmosphere.

The ultimate goal is to develop predictive models for use in emergency preparedness and/or in assessing the environmental and human-health risks associated with energy technologies. The Atmospheric Science Program also promotes the development and transfer of results, models, and new concepts and technologies from research within DOE and industry.

The Department's Environmental Sciences Division (ESD) implements the strategy at the Department's national laboratories, other governmental laboratories, universities, and private industry. The research paradigm includes infrastructure development and science-team elements that provide the intellectual direction for the research and facilitate technology transfer.

PLANNED ACTIVITIES

The Atmospheric Science Program focuses on (1) field activities of the International Global Atmospheric Chemistry Program (IGAC) and the inter-agency Southern Oxidant Study (SOS), (2) the role of aerosols in atmospheric radiation and cloudiness modification, (3) air-surface exchange processes

over land and water, (4) development of advanced boundary-layer and mid-tropospheric chemistry models for interactive chemistry and climate studies, (5) campaigns in complex terrains to examine interactions of local meteorology to meso-scale systems, (6) extending the understanding of scale interactions at the local and mesoscale, and (7) providing advanced predictive capabilities for emergency preparedness at DOE sites.

The Ozone Project, which is included in the Atmospheric Science Program, focuses on improving the estimates of ozone and UV-B trends and on understanding the chemical and dynamical processes that control midlatitude, lower-stratospheric ozone and free-tropospheric ozone in regions remote from major air-pollution sources. This program is conducted in close cooperation with ARM.

PLANNING ASSUMPTIONS

- ▶ The EPACT will require air-quality assessments of the reauthorized Clean Air Act.
- ▶ Safety and health considerations will require improved emergency-preparedness capabilities for accidental releases at DOE sites.
- ▶ Environmental regulations related to energy development will become more stringent. Knowledge of how ecosystems respond to external stresses will contribute to sensible and cost-effective regulatory practices.

PROGRAM SCHEDULE AND PROGRESS

- ▶ Complete the pre-NARE (North Atlantic Regional Experiment) Atlantic campaign and participate in the first phase of IGAC (1993).
- ▶ Complete analysis of the 1992 summer SOS field study (1993).
- ▶ Complete the analysis of data from the Rocky Flats and Oak Ridge studies and quantify the sensitivity of the dispersion models to uncertainties in the source term (1993).

- ▶ Conduct measurement campaigns on air-surface exchange (over land and ocean) for improved parameterizations of these processes in global chemistry models (1994-99).
- ▶ Undertake atmospheric-aerosol studies to elucidate the role of aerosols in cloud and radiative-balance modification (1994-99).
- ▶ Conduct field campaigns at the Colorado Front Range, the Tennessee River Valley, and a coastal location (to be determined) with advanced ground-based remote-sensing instrumentation (1994-99).
- ▶ Transfer computational systems to advanced computers and workstations for real-time emergency-preparedness modeling (1994-99).
- ▶ At ARM sites, initiate UV measurements in cooperation with the U.S. Department of Agriculture (1993-95).
- ▶ Evaluate current ozone databases and incorporate recalibrations of instruments and inves-

tigate data reanalysis to include other possible impacts on the data (e.g., tropospheric aerosols and other regional factors) (1994-99).

- ▶ Initiate modeling studies to understand the sensitivities and uncertainties associated with the chemical-kinetic parameterizations currently being used for simulating the chemistry of ozone formation and destruction in global models (1994-99).

PROGRAM ADMINISTRATION

The Environmental Sciences Division of the Office of Health and Environmental Research, Office of Energy Research, supports the Atmospheric Science Program to contribute to the scientific foundation for the EPACT.

LEVEL OF EFFORT

Research sponsored by the Atmospheric Science Program amounted to \$10,445,000 in FY 1993. The distribution of funds to research areas is presented in Fig. 1.

Fig. 1. Distribution of Atmospheric-Science Funding for FY 1993 in Thousands of Dollars.

ORGANIZATION OF THE PROGRAM SUMMARY

This document provides descriptions for all projects funded by ESD under annual contracts in FY 1993. Each description contains the project's title; three-year funding history (in thousands of dollars); the contract period over which the funding applies; the name(s) of the principal investigator(s); the institution(s) conducting the projects; and the project's objectives, products, approach, and results to date (for most projects older than one year).

Project descriptions are categorized within the report according to program areas: atmospheric chemistry, atmospheric dynamics, and support operations. Within these categories, the descriptions

are ordered alphabetically by principal investigator. Each program area is preceded by a brief text that defines the program area, states its goals and objectives, lists principal research questions, and identifies program managers. Appendixes provide the addresses and telephone numbers of the principal investigators and define the acronyms used.

This document has been indexed to aid the reader in locating research topics, participants, and research institutions in the text and the project descriptions. Comprehensive subject, principal investigator, and institution indexes are provided at the end of the text for this purpose. The comprehensive subject index includes keywords from the Introduction and chapter texts in addition to those from the project descriptions.

ATMOSPHERIC CHEMISTRY

Atmospheric chemistry research within DOE is addressed primarily to the question of atmospheric response to emissions from energy-generation sources. As such, this program deals with all aspects of what is known commonly as the *atmospheric source-receptor sequence*. This sequence consists of all aspects of energy-related pollutants from the time they are emitted from their sources to the time they are redeposited at the Earth's surface.

Because source-receptor transport distances are often large, the interactions between U.S. emissions and those from other countries becomes an important aspect of this overall issue. Recently, many of these aspects have become focused under the EPACT; accordingly, the DOE Atmospheric Chemistry Program (ACP) has been designed to respond directly to agency needs as defined within the EPACT.

Research Objectives. The principal objective of the DOE Atmospheric Chemistry Program is to provide DOE with the advanced information pertaining to the atmospheric environment that is necessary for long-range energy planning in fulfillment of the EPACT. Based on anticipated near- and intermediate-term DOE needs, initial efforts under this program will emphasize the continental and oceanic fate of energy-related air pollutants. This research activity considers all features of the atmospheric source-receptor sequence, including air-surface exchange, heterogeneous and homogeneous air chemistry, and precipitation scavenging.

Research Questions. Accomplishing this objective will require quantitative answers to questions on a

variety of issues. Several of the more important of these issues are outlined below.

Continental issues: energy production's role in

- ▶ Ozone-standard attainment or nonattainment
- ▶ Acidic deposition, both dry and wet, as related to its continental impacts
- ▶ Atmospheric aerosols: PM-10 (particulate matter less than 10 μm) standards and their attainment or nonattainment
- ▶ Effectiveness of future emission regulations in addressing the above issues

Extracontinental and oceanic issues: energy production's role in

- ▶ Multinational contributions to the global pollution pool
  - The North Atlantic
  - The North Pacific
  - The Arctic
  - The significance of former Soviet Bloc and third-world contributions in the context of U.S. and western european energy development
- ▶ Long-range pollutant-transformation processes and their impact on the lifetimes and fates of pollutants
- ▶ Deposition processes and their influences on pollutant lifetimes and fates
- ▶ Natural emissions into the atmosphere and their contributions to the total mixture of atmospheric pollutants
- ▶ Aerosols and their direct influence on the atmospheric radiation balance
- ▶ Aerosols, aerosol precursors, and their effects on cloud formation

Program Manager

Michael R. Riches
Environmental Sciences Division
ER-74
Department of Energy
Washington, DC 20585
301-903-3316

Principal Scientist

Jeremy M. Hales
Envair
4811 W. 18th Ave.
Kennewick, WA 99337
509-735-9480

Research Summaries

MORPHOLOGY-DEPENDENT STIMULATED RAMAN SCATTERING (MDSRS) STUDIES OF GAS-AEROSOL INTERACTION KINETICS

AKER, PAMELA M.

UNIVERSITY OF PITTSBURGH

FY 1993	74
FY 1992	83
FY 1991	0

09/15/93-09/14/94

Objective: To develop the morphology-dependent stimulated Raman scattering (MDSRS) technique to attain significantly increased sensitivity levels.

Product: A measurement technique with which to address the uncertainty in the heterogeneous reactions of pollutants on the surfaces of (or within) aerosol particles.

Approach: This project will develop the MDSRS technique to attain sensitivity levels that are much higher than those of previous measurements. The experimental measurements will apply the enhanced MDSRS technique to measure reaction and/or condensation rates of sulfur and nitrogen gases (SO_2 , DMS, and HNO_3) on the surfaces of water, ice, and sulfuric acid particles. The intensity of Raman scattering is amplified appreciably when the exciting radiation's frequency is near that of an electronic transition. In essence, this sensitivity enhancement will be accomplished by applying shorter wavelength radiation, thereby approaching electronic-transition frequencies.

Results to Date: MDSRS spectroscopy has been demonstrated as an analytic tool for gas-aerosol kinetics studies. The exact analytic form of the nonlinear MDSRS gain equation was elucidated. The reliability of this equation was tested and proved by modeling MDSRS signal strengths observed in a number of spectroscopy experiments. MDSRS sensitivity levels were enhanced over those seen previously by changing the linewidth and wavelength of the excitation laser used in the experiment.

CONTINENTAL AND OCEANIC FATE OF AIR POLLUTANTS

BERKOWITZ, CARL M.

PACIFIC NORTHWEST LABORATORY

FY 1993	525
FY 1992	525
FY 1991	944

10/01/92-09/30/93

Objective: To quantify atmospheric chemical species and atmospheric processes important in energy-related pollutants and to develop a model describing regional-to-hemispheric-scale atmospheric transport, deposition, and chemical reactions.

Product: The atmospheric chemistry information necessary to implement specific requirements of the DOE National Energy Strategy and to guide the progressive modification of the Strategy.

Approach: The PNL Gulfstream-1 (G-1) aircraft will be fitted with a triple quadrupole mass spectrometer to detect and quantify a number of important variables, such as NO_x , NO_y , DMS, acetic and formic acids, peroxyacetal nitrate (PAN), methanol, ethanol, acetaldehyde, acetone, and ammonia, in both polluted and background situations.

The Global Chemistry Model (GChM), a 3-D atmospheric-chemistry model that describes atmospheric transport, deposition, and chemical reactions on scales ranging from regional to global will be developed. Its design will allow for considerable flexibility in the addition or removal of modules describing various physical and chemical processes. The synoptic-scale meteorological fields will be defined by data from a version of the national Center for Atmospheric Research (NCAR) Community Climate Model (CCM); output fields from the CCM, at selected time intervals, will be read by the GChM and used to characterize the wind, temperature, and moisture fields. Emissions input to the model will be read from modified continental and oceanic emission inventories.

Results to Date: Data from the 1992 summer field campaign over the western North Atlantic were analyzed. The layered structure of trace-gas concentrations in and above the boundary layer were described.

During the summer of 1993, PNL participated in the North Atlantic Regional Experiment over the western North Atlantic in conjunction with aircraft from the National Oceanic and Atmospheric Administration (NOAA) and the Atmospheric Environment Service of Canada (AES) and scientists from these agencies and Brookhaven National Laboratory (BNL).

ANALYSIS OF AEROSOL CHEMICAL AND MICROPHYSICAL DATA IN THE NORTH ATLANTIC REGIONAL EXPERIMENT (NARE)

DAUM, PETER

BROOKHAVEN NATIONAL LABORATORY

FY 1993	136
FY 1992	80
FY 1991	0

10/01/92-09/30/93

Objective: To analyze large amounts of data on aerosol microphysical and chemical properties and in the light of this analysis to design and implement an experimental plan for aerosol measurements to be conducted during the NARE program in the summer of 1993.

Product: Analysis of large amounts of data on aerosol microphysical and chemical properties from pre-NARE activities and an experimental plan for aerosol measurements during the North Atlantic Regional Experiment (NARE).

Approach: The primary effort of this project will be to analyze the aerosol data that will be collected during NARE. Such analysis will characterize the spatial distribution and composition of the aerosols, characterize the relationship between sulfate mass concentration and aerosol number densities, and examine the relationship between pre-cloud aerosol number concentrations and cloud droplet concentrations in marine stratus clouds.

Results to Date: The pre-Nare field campaign was conducted in late summer 1992. A filter sampling system for collection of aerosols for subsequent analysis was deployed as part of this project, and 29 samples were

collected. These samples were analyzed in the laboratory for the ammonium, sulfate, and nitrate contents of the aerosol.

Concentrations of these aerosol constituents varied widely, both as a function of meteorological back trajectory and as a function of the altitude. Concentrations of aerosol sulfate and nitrate ranged between their nominal detection limits of $0.1 \mu\text{g}/\text{m}^3$ and concentrations in excess of $25 \mu\text{g}/\text{m}^3$. The highest concentrations were observed in air masses that had been transported from the south and southwest; the lowest concentrations were observed in air masses that had been transported from the north. The aerosol particles seem to have been transported in layers, mainly at altitudes above 3000 ft. The reason for this layering is not clear and will be the subject of subsequent analysis.

CONTINENTAL AND OCEANIC FATE OF ENERGY-RELATED AIR POLLUTANTS

DAUM, PETER; NEWMAN, LEONARD;
LEE, YIN-NAN; and KLEINMAN, LAWRENCE I.

BROOKHAVEN NATIONAL LABORATORY

FY 1993	950
FY 1992	1200
FY 1991	1300

10/01/92-09/30/93

Objective: To obtain data and to develop models to understand the atmospheric processes that control the transport, transformation, and ultimate fate of energy-related air pollutants.

Product: The determination of the fate of energy-related air pollutants, with emphases on the fate of sulfur and nitrogen compounds and on the oxidants that can influence their behavior.

Approach: Measurements will be made by aircraft under a variety of clear-air conditions (1) to measure the vertical profiles of various classes of compounds (including nitrogen species, sulfur species, secondary photochemical pollutants, aerosols, and water) to develop an understanding of the influence of redistributed species on free tropospheric chemistry and (2) to develop a climatology of vertical distributions of pollutants exiting eastern North America to the North

Atlantic and to relate features of this climatology to synoptic conditions and chemical history.

A systematic series of measurements by aircraft in clouds will be performed to study the influence of pre-cloud particle-number concentrations on nucleation scavenging efficiency, to study cloud-droplet composition as a function of droplet size, to identify reactive scavenging mechanism for nitrogen oxides, and to study properties of organic aerosols as cloud condensation nuclei (CCN).

Laboratory studies will be conducted to better elucidate both photochemical reactions of pertinence to transport and redistribution of materials and to the transformation and removal of species by aqueous-phase reactions. The first task includes laboratory studies of the photochemistry of organic product species that have long but uncertain lifetimes and are expected to have a global impact, such as organic nitrates, organic peroxide, and carbonyl compounds. The objectives of the latter task are to identify the significant chemical-reaction pathways taking place in aqueous solutions that are responsible for the enhanced uptake of important atmospheric species by liquid water and to determine the respective rate laws, rate coefficients, and stoichiometries of those reactions. Laboratory data will be combined with field data, such as ambient reagent concentrations, and will be incorporated into diagnostic models for evaluation of various processes leading to the transport and deposition of pertinent species.

Diagnostic modeling studies will be designed to provide a consistent framework to synthesize and interpret observed data and to provide input for construction of large-scale models. Results of these diagnostic modeling studies will be used to guide more-extensive calculations and to design components of future field programs.

Results to Date: Analysis of the data collected during the DOE/ACP field study of the Kuwait oil-fire plume in mid-summer of 1991 was completed. During this study, the plume was transported almost exclusively to the south of Kuwait over the Persian Gulf and the Arabian Peninsula. The plume base was generally well above the surface, in some cases as high as 1 to 2 km; plume tops did not exceed 5 km. Aerosol mass (based on measured aerosol constituents) in the central section of the plume close (within 100 km) to the source was found to be $> 500 \mu\text{g}/\text{m}^3$. The aerosol was composed of (in the order of approximate contribution to mass) inorganic salts, elemental carbon, and organic carbon.

Sodium chloride comprised a surprisingly large ($>20\%$) component of the soluble inorganic mass. The aerosol particles appeared to function as good CCN, with a large fraction of accumulation-mode particles (by number) activated at a supersaturation of 0.6%. Where the plume was relatively compact, transmittance of solar radiation to the surface was only 10 to 20%. Plume albedo was observed to be as low as 2% close to the source region, consistent with the high elemental-carbon concentrations present in the plume. Trace-gas concentrations were consistent with fuel composition and with current knowledge of atmospheric-chemistry processes. The emissions factor for sulfur was estimated to be 1.8%, consistent with estimates of a fuel sulfur content of 2 to 2.5%. SO_2 was found to be only slowly oxidized ($<1\%/h$). Nitrogen-oxide concentrations were found to be quite low (<50 ppb near the source, decreasing to 1 ppb well downwind), consistent with a crude-oil nitrogen source. Despite the relatively low concentrations, sufficient NO_x was present to act as a catalyst to produce excess ozone in the plume as it was transported downwind and dispersed.

MEASUREMENT OF GAS-WATER UPTAKE COEFFICIENTS FOR TRACE GASES ACTIVE IN THE MARINE ENVIRONMENT

DAVIDOVITS, PAUL

BOSTON COLLEGE

FY 1993	111
FY 1992	106
FY 1991	101

08/01/93-07/31/94

Objective: To measure air-water exchange coefficients of specific gases that are of importance in the marine atmosphere.

Product: Measurements of the interphase transport of trace gases between the gaseous and aqueous phases, which represents an important internal calculation in atmospheric chemistry models.

Approach: Measurements of uptake coefficients on aqueous droplets will be performed for reduced sulfur species, including dimethyl sulfide (DMS), hydrogen sulfide, carbon disulfide, methyl mercaptan, and their oxidation products, including carbonyl sulfide, methane sulfonic acid (MSA), dimethyl sulfoxide (DMSO), and

dimethyl sulfone (DMSO₂). The uptake coefficients will be measured over a sufficient range of conditions to provide both the mass-accommodation coefficient and the solubility parameters for these species. Measurements will be made as functions of temperature, pH, and ionic strength.

Measurements of uptake coefficients on aqueous droplets will be performed for ozone, NO, NO₂, and NO₃. As with reduced sulfur above, measurements will be acquired over a range that will provide both the mass-accommodation coefficient and the solubility parameters for these species. Measurements will be made as functions of temperature, pH, and ionic strength.

Results to Date: The mass-accommodation coefficients were measured for the soluble-sulfur compounds DMSO, DMSO₂, and MSA as a function of temperature, pH, and NaCl concentration. These experiments were done with the droplet apparatus, which is characterized by short (1- to 10-ms) gas-liquid contact time. Longer gas-liquid interaction times have to be used to study the interactions of the less-soluble gas-phase species. During the past year, a new bubble-column apparatus has been developed to study the kinetics of gas-liquid interactions for species with low uptake coefficients in the range 10⁻⁴ to 10⁻⁸. An analysis of the gas-uptake measurements yields values of Henry's Law coefficients and interfacial or bulk-phase reaction rates for the species. The apparatus has been thoroughly tested with species with known parameters. Gas-liquid interaction and codeposition studies are now in progress for O₃, DMS, and NO₂.

ATMOSPHERIC TRACER AND INSTRUMENTATION DEVELOPMENT

DIETZ, RUSSELL N.

BROOKHAVEN NATIONAL LABORATORY

FY 1993	220
FY 1992	220
FY 1991	220

10/01/92-09/30/93

Objective: To identify and use new atmospheric tracer compounds for long-range transport studies and to support these studies through the development, validation, and application of new instrumentation.

Product: The development and application of unique, highly sensitive detection methods and instrumentation to determine trace constituents in the atmosphere, specifically perfluorocarbon tracers (PFTs).

Approach: Techniques, methods, and instruments will be produced that are needed and are immediately useful to programmatic tracer-technology efforts at BNL and other agencies. The commercialization of those instruments especially valuable to a large number of potential users will be implemented. The value of tracer technology will be developed and demonstrated in numerous government and commercial applications. Field experiments will be performed to verify the reliability and usefulness of all developments.

Results to Date: Improvements have been made to the three PFT analytical systems. A commercial carbon layer open tubular (CLOT) capillary column was shown to improve peak resolution about five-fold; this means that tracer costs for a multitracer long-range or complex-terrain atmospheric-transport and -dispersion test can be reduced by 80%. Higher-capacity adsorption traps (up to 5L/min of sampling air) have been installed in the dual-trap analyzer (DTA) to increase PFT detectability [e.g., ocPDCH (ortho(cis)-perfluorodimethylcyclohexane) at an ambient concentration of 0.35 x 10⁻¹⁵L/L] in a 3- to 4-min cycle time. Even higher-capacity traps (up to 12 L/min) have been rapidly desorbed by direct ohmic heating, itself a potential new technology. A prototype of a new commercial version of the BNL DTA will be constructed.

ATMOSPHERIC CHEMISTRY OF ORGANIC OXIDANTS AND ALDEHYDES

GAFFNEY, J. S., and MARLEY, N. A.

ARGONNE NATIONAL LABORATORY

FY 1993	180
FY 1992	180
FY 1991	180

10/01/92-09/30/93

Objective: To obtain fundamental information regarding the chemical and physical properties, tropospheric concentrations, seasonal variability, and sources of organic oxidants, organonitrates, and aldehydes.

Product: A database for organic oxidants, organonitrates, and aldehydes allowing improved evaluation of their roles in air quality and as greenhouse gases.

Approach: An interactive research effort involving field measurements, laboratory studies, modeling, and, as necessary, analytical technique development will be used. The potential roles of natural hydrocarbons interacting with energy-related oxides of nitrogen and sulfur dioxide emissions will be evaluated with regard to the formation of organic oxidants and aerosol species. The potential impacts of increased ultraviolet type-B (UV-B) radiation on the photochemical production of these species in the troposphere will also be assessed.

Results to Date: Peryoxyacetyl nitrate (PAN) and ozone data taken at a remote site near Los Alamos, New Mexico, have shown that PAN levels and ozone levels are correlated with temperature and anticorrelated with each other. These observations indicate that PAN levels will be higher on regional levels during colder periods, while ozone will increase under warmer conditions. The roles of natural hydrocarbons in the production of tropospheric oxidants and in sulfate formation continue to be examined; studies indicate that the interaction of energy-related NO_x emissions and isoprenoid organics plays an important role in regional pollution and climate. Cylindrical internal reflectance and thin-film Fourier-transform infrared (FTIR) spectroscopy have been used to evaluate dissolved inorganic and organic species as infrared absorbers in aerosol, fogs, and clouds. The infrared absorption of liquid water has also been reexamined in the region of 800 to 3000 cm^{-1} . The results indicate that the absorption of infrared radiation by aerosols, particularly sulfate, may counterbalance the light-scattering effects in the troposphere. Laboratory studies examining UV-B radiation effects on dissolved organics have been initiated.

ARCHIVING AND ANALYSIS OF THE ATMOSPHERIC MEASUREMENTS OF SMOKE FROM THE KUWAIT OIL FIRES

GREENFIELD, RICHARD S.

NATIONAL SCIENCE FOUNDATION

FY 1993	65
FY 1992	0
FY 1991	150

09/15/93-09/14/94

Objective: To archive all atmospheric chemistry and meteorological data taken in the Persian Gulf region during the Kuwait oil fires so it can be provided to the scientific community.

Product: An integrated data set for the scientists of the world from one central archive.

Approach: The data include ground-based, aircraft, and satellite observations. Elements include standard meteorological data as well as in situ and remotely sensed atmospheric chemical and physical characteristics of the fire plumes. The documentation for the data sets obtained by the international research effort on the oil fires will be cataloged and assembled. An archiving method appropriate to the data set will be developed, and accessibility will be optimized. The final archive and central data center will be established and will include international dissemination of the data. Specific analytical tools will be developed to assist in extracting, browsing, and displaying the integrated data set.

POLLUTANTS IN DEPOSITION AND THE BIOSPHERE

HEIT, MERRILL

ENVIRONMENTAL MEASUREMENTS LABORATORY

FY 1993	1334
FY 1992	1634
FY 1991	1634

10/01/92-09/30/93

Objective: To determine the environmental history (concentrations, magnitude, fluxes, trends, and inventories) of energy-produced pollutants (potentially toxic to humans and biota) deposited in selected regions and ecosystems of the contiguous U.S. and of the Alaskan and Russian Arctic.

Product: An understanding of the environmental fate and prediction of future depositional trends for pollutants associated with the release of energy-related pollutants (including radioactivity) into the atmosphere.

Approach: The depositional histories of energy-related, potentially carcinogenic organics, radionuclides, and toxic metals will be determined for lakes and watersheds located in selected sites within the contiguous U.S., such

as the Finger Lakes Region of New York and the Olympic Peninsula in Washington. Investigations related to arctic haze will be conducted in the Taymyr and Kola peninsulas of Russia and in the Brooks mountain range and coastal plain regions of Alaska, locations likely to be excellent receptors of long-distance, atmospherically transported pollution.

Information on pollutant deposition will be obtained by reconstructing pollutant histories from the records preserved in lake sediments, often a significant repository for atmospherically transported materials entering the environment. The sediments will be dated by measurements of their artificial and natural radioactivity and by various nonnuclear techniques.

Other environmental matrixes will be sampled to aid in the investigation of atmospherically transported contamination. Alaskan and Siberian soil samples, for one, may provide the best estimate of the inventories of various deposited pollutants related to arctic haze. A more novel approach to these arctic studies will involve the use of lichen and moss samples as surrogates of deposition because they may accumulate substances directly from the atmosphere or from materials deposited on them.

Results to Date: Sediment cores have been collected from four lakes on the Olympic Peninsula just east of the vast expanse of the North Pacific Ocean, where air masses are thought to be relatively quite clean. Mercury concentration profiles in the radionuclide-dated sediment cores nevertheless indicate that significant increases in Hg inputs have occurred at all four lakes during the twentieth century. Previously reported trends in Pb deposition are similar, indicating that even in this relatively pristine environment the biogeochemical cycles of trace substances can be significantly altered by atmospheric transport of pollutants emitted from more heavily industrialized regions.

Analytical results for Pb, Zn, Cu, and Cd in Seneca Lake in the Finger Lakes district indicate that atmospheric deposition rates of all four elements rose detectably above natural background levels prior to 1900, increased dramatically during the twentieth century, reached peak values in the late 1960s and early 1970s, and declined substantially since then. The trends in atmospheric deposition of these four elements corroborate fairly well the estimates of historical atmospheric emissions trends that have been derived from U.S. primary production and emission-control data.

A variety of environmental samples (lake sediments, soils, lichens, and mosses) have been collected to investigate the source, magnitude, spatial extent, and deposition history (flux and inventory) of contaminants in the arctic. Recent results for PAH and polychlorinated dibenzo-dioxin (PCDD) and -furan (PCDF) analyses of Wonder Lake sediment (central Alaska) show that all concentrations and reconstructed fluxes are quite low except for perylene and some other PAHs that are formed from natural products. The concentrations of PAH and PCDD/PCDF also do not vary greatly throughout the sediment. Because of the very low levels, and uniform distributions with depth, the primary source of combustion-produced PAH and PCDD/PCDF into Wonder Lake is suspected to be natural processes (fires) rather than anthropogenic combustion.

ATMOSPHERIC ORGANIC CHEMISTRY: INVESTIGATION OF PRIMARY AND SECONDARY SPECIES

LEE, YIN-NAN

BROOKHAVEN NATIONAL LABORATORY

FY 1993	260
FY 1992	260
FY 1991	260

10/01/92-09/30/93

Objective: To obtain an increased understanding of the distribution, transformation, and fate of atmospheric organic compounds and to obtain a better understanding of the involvement of organic compounds in atmospheric nitrogen and oxidant cycles.

Product: An understanding of the atmospheric photo-oxidation pathways of organic compounds to assess their importance in regional oxidant formation (and therefore acid deposition), possible health and phytotoxic effects, and global atmospheric chemistry.

Approach: The research will involve both laboratory and field studies of the compounds and processes of interest. Existing techniques, where available, will be adapted and refined for the proposed atmospheric measurements, and measurement techniques not available will be developed. Sampling, separation, and analysis techniques will be developed and validated as required.

Synthesis and characterization of product compounds will be carried out in cases where sources are not available. Laboratory determination of the photolysis rate of organic nitrates will be accomplished with techniques developed previously for the study of peroxyacetal nitrate (PAN). Additional techniques will be developed to measure temperature dependencies of absorption cross-sections and the quantum efficiencies for photodissociation of these species. Field measurements will be conducted in conjunction with larger experiments at surface sites and on aircraft platforms. The experimental techniques used will include packed-column and capillary gas chromatography (GC) with selective and sensitive detectors, such as mass spectrometry, electron capture, photoionization, and flame ionization detection. High-pressure liquid chromatography with fluorescence and UV detection will also be employed in the measurement of aldehydes. FTIR and UV-vis spectroscopic methods will be used in laboratory studies. Ancillary techniques to be applied to the characterization of synthesis products will include MS and ^1H , ^{14}N , and ^{15}N nuclear-magnetic-resonance spectroscopy. A variety of sampling and standards preparation methods will be evaluated to achieve necessary sample integrity and overall accuracy and precision. Intercomparisons will be sought of methods and standards used in this work with those employed by other researchers working in these areas.

Results to Date: We measured the concentrations of a number of photochemically reactive compounds during two field intensives at Metter, Georgia, during the summers of 1991 and 1992. For carbonyls, the maxima in ppb, were:

Species	Concentration (ppb)
Formaldehyde (C1)	8
Glycolaldehyde (HC2)	2
Methylglyoxal (Mgl)	0.3
Glyoxal	0.1
Glyoxylic acid	3
Pyruvic acid	0.3
Acetaldehyde (C2)	2
Acetone	4
Propionaldehyde	0.5

These results represent the first identification of HC2 and glyoxylic acid. The contribution to free-radical production from the rest of the carbonyls is as much as

50% of that by C1. Mgl contributes up to 50% of the peroxyacetyl radicals and is an important precursor of PAN. The average NO_y ($= \text{NO} + \text{NO}_2 + \text{HNO}_3 + \text{PAN} + \text{aerosol nitrates}$) concentrations, 1.6 and 2.4 ppb for 1991 and 1992, respectively, were fairly constant diurnally. Because the missing organic NO_y exhibited no diurnal dependence, multifunctional organic nitrates, such as α -hydroxynitrates, may not be the dominant components.

We determined in the laboratory a rate constant of $4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ (15.0°C) for the aqueous O_3 -DMS reaction. The implications are that the atmospheric lifetime of DMS against the in-cloud O_3 -DMS reaction at 30 ppb of O_3 and 1 g/m^3 of liquid water is comparable to that against the gas-phase OH reaction and that the deposition of O_3 to the ocean surface is not enhanced by this aqueous reaction.

ATMOSPHERE-CANOPY INTERACTIONS

LINDBERG, STEVEN E.

OAK RIDGE NATIONAL LABORATORY

FY 1993	200
FY 1992	200
FY 1991	200

10/01/92-09/30/93

Objective: To quantify rates of wet and dry removal processes and surface emission rates of both natural and pollutant constituents important to atmospheric chemistry and to biogeochemical cycling in forests.

Product: A verified model and database capable of describing the fate of both natural and pollutant constituents in forest canopies.

Approach: The rates and mechanisms of deposition to the forest canopy of trace elements involving vapor phase reactions in coal combustion emissions will be investigated to improve our understanding of the atmosphere-landscape portion of the biogeochemical cycles of Hg, Se, and As through studies of the roles of wet and dry deposition of the important chemical species of these elements. The work will initially emphasize Hg because of existing expertise, and will involve measurement of concentration gradients at the Walker Branch site, development of a dry-deposition model from canopy-resistance approaches, and analysis of wet

deposition and its interaction with the forest canopy. This research will capitalize on recently developed analytical capabilities for picogram-level analysis and chemical speciation. We have obtained cofunding from the Electric Power Research Institute to expand these studies with the application of chamber and micrometeorological methods to both deposition and emission measurements at high- and low-elevation sites. This work will be a joint effort with researchers at the National Oceanic and Atmospheric Administration (NOAA) Atmospheric Turbulence and Diffusion Division (ATDD) lab and the Swedish Environmental Research Institute in Göteborg.

An approach for scaling up air/surface exchange measurements will be developed based on surface analysis methods. A model will be developed to analyze throughfall (TF) beneath forests which separates net TF (TF flux minus rain flux) into its component parts of foliar leaching and dry-deposition washoff. The model will require single-event TF data collected over one season. The model will be applied to data from two sites: a low-elevation loblolly pine plantation near Oak Ridge, Tennessee (300-m elevation), and a high-elevation red spruce stand in the Great Smoky Mountains National Park (1740 m). Precipitation will be collected in forest clearings and beneath the canopy as wetfall-only on an event basis. Replicate TF collectors will be used to establish the spatial variability of net TF fluxes within the stands. Six permanent collectors will be established at the pine site, and two at the remote mountain site. Additional intensive collection grids of 20 collectors will be used for selected events to determine the representativeness of the permanent sampling points. The sites will include a meteorological tower extending approximately 10 m above the forest canopy and will be instrumented with standard meteorological sensors for continuous recording.

Total deposition and canopy exchange will be measured in a high-elevation spruce canopy, and edge effects and gap depositions will be quantified. This task will measure total flux of atmospheric and internal materials above and below the canopy, in the same fashion as done earlier for the deciduous canopy to address the question of the role of dry deposition in controlling the chemistry of throughfall. The methods will be applied to a newly established spruce stand at 1740-m elevation in the Great Smoky Mountains National Park. A meteorological tower has been established. The new site is considerably removed from the influence of the local DOE and Tennessee Valley Authority (TVA) coal-fired

power plants and consists of a typical, heterogeneous spruce canopy consisting of numerous gaps and edges.

The chemistry of fog and cloud water will be studied in high and low elevation forests by collecting fog and cloud water at the new loblolly pine site and at the new spruce site in the Smoky Mountains for the purpose of comparing the chemistry of these solutions and, ultimately, the fluxes to each forest determined by a resistance model. Fog and cloud droplets will be sampled with a combination of passive harp-type and active impaction-type collectors operated above the canopy.

Results to Date: To test the applicability of micrometeorological methods for estimating the atmosphere-surface exchange rates of elemental mercury (Hg^0) in the vapor phase, we estimated Hg^0 emissions over contaminated soils near Oak Ridge using concentration gradients with the modified Bowen ratio method. We designed and built a sampler for Hg^0 that uses a single vacuum pump connected via a manifold to six separate mass-flow controllers. We routinely achieve precision for six replicate measurements of Hg^0 in background air of 0.5 to 2% (with concentrations of <1 pptv). Our measurements indicate that the contaminated soils acted as a source of Hg^0 to the atmosphere with source strengths 1 to 2 orders of magnitude above emissions from background soils. The Hg^0 emissions were strongly related to surface soil temperature, residence time of air masses over the source area, and turbulence conditions.

ATMOSPHERIC AEROSOL MICROPHYSICS FORMATION, CHARACTERIZATION, AND INTERACTION

MARLOW, WILLIAM H.

TEXAS ENGINEERING EXPERIMENT STATION/TEXAS A&M

FY 1993	108
FY 1992	108
FY 1991	107

09/01/93-08/31/94

Objective: To develop the theoretical and mathematical foundations for describing the formation and metamorphosis of ultrafine aerosol particles (i.e., those up to 50 nm in radius).

Product: A reduction in the uncertainty associated with the modeling of the effects of air pollution.

Approach: The roles of equilibrium vapor pressure and kinetics in water condensation on an aerosol will be studied. One case that will be investigated is that of a pair of adhering spheres (as in aerosols produced by fires). Where the spheres are in contact, the water-air interface may well have a negative overall curvature (i.e., it is concave), thus enhancing condensation.

To explain the aerosol activation spectrum under transient supersaturation conditions (such as occur in cloud nucleation), the background vapor pressure will be coupled to the overall thermodynamic conditions (vapor depletion, latent heat release, etc.) and the particle equilibrium vapor pressure.

Because of the following considerations, accurate, computationally practical schemes for the determination of these interaction energies will be developed.

- ▶ The interaction energies of particles are important (1) for the determination of their collisional growth rates, (2) possibly for the determination of the shapes of aggregates, and (3) for the evolution of their shape under condensation-evaporation cycles.
- ▶ The interaction energy of a condensing fluid with a condensation substrate determines the shape of the condensed fluid.
- ▶ That shape largely determines the equilibrium vapor pressure over the particle.

Particular attention will be paid to the approach that starts from the Lifshitz-van der Waals theory for long-range intermolecular forces of a continuum or condensed matter.

Results to Date: Calculations have been performed of the equilibrium vapor pressures of water in the presence of adhering 50-, 100-, and 200-nm radii spherical particles with water-substrate contact angles ranging from 0 to 85°. The results indicate that, in this range, a drastic reduction occurs in the equilibrium vapor pressure relative to the single sphere. At subsaturation humidities, some water is always associated with these particles. For example, for moderately hydrophobic 100-nm spheres on which water has a 70° spreading angle, unconstrained condensational growth is predicted for a supersaturation of only 1%. This indicates the capability

of chained, moderately hydrophobic particles to serve as cloud condensation nuclei and to otherwise participate in atmospheric light scattering and absorption.

The collective, long-range, intermolecular interaction potentials between particles smaller than 10 nm are the subject of calculations now in progress. The simple point-dipole approximation for calculating spectral retardation of the potential has been shown to be surprisingly accurate, and comparisons of various forms of the potentials have been made. These results, and others, are being used in studies of the force between a single sphere and a pair of adhering spheres in various orientations.

ULTRAFINE-AEROSOL SIZE DISTRIBUTIONS AND SULFURIC ACID VAPOR PRESSURES: IMPLICATIONS FOR NEW PARTICLE FORMATION IN THE ATMOSPHERE

McMURRY, PETER H.

UNIVERSITY OF MINNESOTA

FY 1993	95
FY 1992	93
FY 1991	94

08/01/93-07/31/94

Objective: To determine production rates of new sulfuric acid particles by homogeneous nucleation.

Product: An improved understanding of the relationship between atmospheric emissions (especially aerosol precursor gases) and atmospheric-aerosol size distributions.

Approach: The experimental program will focus on two key measurements. The first of these involves measurement of the vapor pressure of sulfuric acid at temperatures and relative humidities relevant to the atmosphere. Vapor pressures will be inferred from measured evaporation rates of monodisperse ultrafine (5- to 50-nm-diam) sulfuric acid droplets. The tandem differential mobility analyzer (TDMA) technique will be used for these measurements. This method is especially suitable for measuring ultralow vapor pressures and has been used successfully with other species. The sulfuric acid vapor pressure is a key variable for determining nucleation and growth rates.

The second key measurement pertains to the size distribution of ultrafine aerosols. The ultrafine aerosol condensation nucleus counter (UFACNC) of Stolzenburg and McMurry will be used for these measurements. Proposed measurement techniques involve measuring the UFACNC pulse-height distribution as a function of particle size and varying the size-dependent cut point of the instrument by adjusting its condenser temperature. The ultrafine aerosol-particle distributions thus obtained will provide important information on rates of homogeneous nucleation.

Results to Date: A joint field study involving atmospheric measurements of expected homogeneous nucleation precursors and aerosols was conducted at the Mauna Loa Observatory, Hawaii, from June 28 to July 28, 1992. Free tropospheric air masses were found to have the highest concentrations of MSA but low concentrations of ultrafine particles (between approximately 3 and 7 nm in diameter), whereas boundary-layer air had the highest H_2SO_4 and ultrafine-particle concentrations.

Total aerosol surface area and H_2SO_4 concentration had strong influences on ultrafine-particle concentrations, while temperature and relative humidity did not. The data indicate that H_2SO_4 was the likely precursor of the newly formed particles, whereas MSA contributed little.

Approximately 65% of the time, ultrafine-particle concentrations in boundary-layer air were between 0.1 and 10 cm^{-3} . This prevalence of ultrafine particles may indicate the presence of a widespread low-nucleation-rate source of new particles that may play an important role in maintaining background aerosol concentrations.

A new instrument intended to measure size distributions of particles in the 3- to 7-nm-diam range with better accuracy is under construction. Such measurements done in parallel with measurements of gas-phase precursors will permit the measurement of instantaneous ultrafine-particle source rates.

**PARTIAL SUPPORT FOR THE 1993 GORDON
RESEARCH CONFERENCE ON
ATMOSPHERIC CHEMISTRY AND A
COMPANION MEETING FOR NEW
ATMOSPHERIC CHEMISTRY RESEARCH
SCIENTISTS**

MOYERS, JARVIS L.

NATIONAL SCIENCE FOUNDATION

FY 1993	15
FY 1992	0
FY 1991	0

06/15/93-06/14/94

Objective: To support the 1993 Gordon Research Conference on Atmospheric Chemistry and the Atmospheric Chemistry Colloquium for Emerging Senior Scientists (ACCESS).

Product: Opportunities for scientists to discuss predicting atmospheric change and for selected graduate students and postdoctoral students to present their research results to agency representatives and senior scientists.

Approach: The National Science Foundation, National Aeronautics and Space Administration, National Oceanic and Atmospheric Administration, and Department of Energy will jointly support two conferences, the Atmospheric Chemistry Colloquium for Emerging Senior Scientists (ACCESS II) and the 1993 Gordon Conference on Atmospheric Chemistry. At ACCESS II, approximately 35 selected senior graduate students and postdoctoral students will present the results of their current research to build a sense of peer community among the young atmospheric chemists and to introduce them to the major federal atmospheric chemistry programs. Agency representatives will provide brief overviews of their research programs, including goals, foci, and funding opportunities.

About 135 leading atmospheric scientists and students will participate in the 1993 Gordon Research Conference, which will cover atmospheric chemistry: observations, models, and prediction; laboratory studies; atmospheric measurements; scientific assessments; future directions; and global connections. Tropospheric and stratospheric chemistry will be addressed in each session.

AEROSOL AND CLOUD CHEMISTRY

NOVAKOV, TIHOMIR

LAWRENCE BERKELEY LABORATORY

FY 1993	100
FY 1992	156
FY 1991	100

10/01/92-09/30/93

Objective: To experimentally investigate the chemical and physical processes involved in aerosol-gas-cloud interactions.

Product: An understanding of the relationship between cloud microphysical properties and heterogeneous aqueous chemical reactions and empirical data on aerosol carbon scavenging.

Approach: This study will involve laboratory experiments, instrumentation development, and interlaboratory collaborations in modeling and theoretical studies.

The principal tool for the laboratory experiments will be the cloud chamber, which enables simultaneous measurement of the chemical composition of cloud water and interstitial aerosols and the condensation properties of aerosols used to nucleate the cloud.

Cloud formations are induced by two modes of operation. In the first, the dilution cold air is kept at a constant low temperature, and the dew point of the sample air is increased by increasing the temperature of the humidifier. When the mixture dew point exceeds the mixture temperature, the cloud is formed. Alternatively, the sample-stream dew point is kept constant, and the temperature of the dilution air is lowered. In this second mode of operation, the total water content in the system is constant, which is particularly suitable for studying the effect of water phase change on the chemistry.

The temperature and humidity fields resulting from the turbulent mixing of the two air flows in the chamber determine the initial supersaturation of water vapor, although the effective supersaturation on a microscale depends on the particle nature and concentration. As the air mixture becomes supersaturated, an increasing number of particles will reach the unstable growth regime.

Nucleation and droplet growth then rapidly remove excess water vapor from the system and reduce the supersaturation to less than that expected for the mixing of particle-free air streams.

Aerosol particles to serve as cloud condensation nuclei will be introduced together with humidified air through the input at the chamber base. A unique feature of this experimental facility is the application of a two-channel aethalometer, and LBL-developed instrument for monitoring black-carbon concentrations in real time. This instrument will be used to measure the black-carbon particles that are incorporated in cloud drops and those that constitute the interstitial aerosol. This measurement will be achieved by using one channel for detecting particles less than $23\text{ }\mu\text{m}$ (interstitial aerosol) and the other channel for measuring total droplets without a size cutoff. This difference between the two channels is equal to the carbon concentration incorporated in cloud drops. This procedure will give a direct measurement of the nucleation properties of soots.

Results to Date: The reaction of NO_2 with liquid water has been studied with cloud-chamber and water-bubbler experiments. The data indicate:

- ▶ The reaction is first-order with respect to NO_2 for both phase-mixed and mass-transport-controlled reaction regimes.
- ▶ The reaction of NO_2 with acidified droplets is a source of gaseous nitrous acid.
- ▶ The HNO_3 dissolved in water droplets enhances the uptake and oxidation of NO_2 .

New laboratory experiments were initiated on the nucleation properties as a function of particle size and with supersaturation ranging from 0.2 and 1.3%. In these experiments, commercial carbon blacks have been used as well as soot particles produced by combustion of diesel fuel. Ammonium sulfate and sodium chloride were used as reference aerosols. The surface chemical properties of carbon blacks were chemically modified by treatment with sulfuric and nitric acid, and the diesel soot was modified by adding thiophene to the fuel. The results of these measurements show that, by chemically modifying the surfaces of carbonaceous particles, their nucleation properties could become similar to those of water-soluble particles.

**MODELING IN SUPPORT OF DOE'S
PARTICIPATION IN THE NORTH ATLANTIC
REGIONAL EXPERIMENT**

PENNER, JOYCE E.

**LAWRENCE LIVERMORE NATIONAL
LABORATORY**

FY 1993	100
FY 1992	156
FY 1991	0

10/01/92-09/30/93

Objective: To use tropospheric chemistry models in support of the Pacific Northwest Laboratory G-1 aircraft measurements in the North Atlantic Regional Experiment.

Product: The ability to predict oxidant concentrations in the troposphere resulting from energy-related pollutants.

Approach: Before the experiment, model estimates of the expected abundance of NO, NO_x, HNO₃, DMS, SO₂, and aerosol will be made with meteorological fields from the LLNL-version of the NCAR general circulation model, CCM1. Within the constraints of the ability to complete the development of the nucleation model, model estimates of the vapor phase of H₂SO₄ and aerosol number concentrations may be provided. These estimates will be focused on the region of the G-1 flights. Because these flights are close to the source regions and because the model may inaccurately portray these regions, a number of sensitivity studies will be carried out to compare the predictions of the model for this region with different numbers of parcels, different mixing coefficients, and different algorithms for mapping concentrations from the Lagrangian parcels (which are computed by the models) to concentration ratios on the Eulerian grid.

Following the G-1 experiments, predictions of the model will be compared with the data collected by the G-1 and by other groups participating in NARE. If possible, this comparison will be done with realistic meteorology that is specific to the timeframe of the measurements. This model/data comparison will be used to check the consistency in understanding the sources, transport, transformation, and loss processes of the trace species

involved in the formation of atmospheric oxidants and sulfate aerosol. The comparison will also be used to help plan a more comprehensive field experiment in the future.

Results to Date: A simulation of the tropospheric oxidant cycle was completed that included the chemistry of CH₄, CO, and the nitrogen oxides. The predictions from this model were compared with data and were, in general, low. This result indicates the need to include the chemistry of nonmethane hydrocarbons (NMHCs). A perpetual-July simulation was completed that included the emissions and oxidation of isoprene, a naturally occurring NMHC. Ozone concentrations in this model were increased relative to those in the model that included only CH₄ and CO, and the results showed that NO_x concentrations at remote ocean locales could also be increased because of the formation of peroxyacetyl nitrate and its long-range transport. The model results for ozone are still low. The effects of anthropogenic NMHCs will be examined next. Model simulations of SO₂ and sulfate aerosol concentrations were also completed, and the latter were compared to data.

AEROSOL CHEMISTRY AND DYNAMICS

TANG, IGNATIUS N.

BROOKHAVEN NATIONAL LABORATORY

FY 1993	260
FY 1992	260
FY 1991	260

10/01/92-09/30/93

Objective: To elucidate the chemical and physical processes governing the formation and dynamic behavior of ambient aerosols.

Product: A clear understanding of the basic mechanisms by which pollutants from energy-related activities may transform and transport in the environment; the thermodynamic and optical data on aerosol particles needed as input to mathematical models describing important atmospheric processes, such as acid precipitation and radiation balance.

Approach: Experiments will be carried out with single aerosol particles suspended in a laser beam by a

quadrupole particle trap. The trap will be contained inside a water-jacketed vacuum chamber that can be pumped down to 10^{-7} torr and backfilled with reactive gases at controlled pressures. Both gravimetric and optical measurements can be made with a levitated particle either undergoing reaction or at equilibrium with the surrounding gaseous medium. Theoretical work on aerosol phase transformation and particle-gas reactions will also be developed for systems of atmospheric importance.

Results to Date: Experiments were carried out to investigate aerosol deliquescence properties in the temperature range of 5 to 35°C with the single-particle-levitation technique described above. Results were obtained for particles containing either a single salt or a pre-selected mixture of NaCl, KCl, NaNO₃, Na₂SO₄, and (NH₄)₂SO₄, which are common constituents of ambient aerosols. A theoretical model for the composition and temperature dependence of the deliquescence properties was developed for single- and two-salt aerosol systems. Parameters required in the equations were derived from literature data on the heats of solution and the solubilities of the salts and salt mixtures. Excellent agreement was obtained between theory and single-particle measurements. Additional work was also done to extend previous studies to include aerosol particles containing more than two salts. It was seen that the system is too complex for the current theoretical analysis and that further work is needed to elucidate and predict the complex nature of multicomponent aerosols.

ATMOSPHERIC PEROXIDES

WEINSTEIN-LLOYD, JUDITH B.

STATE UNIVERSITY OF NEW YORK/COLLEGE
AT OLD WESTBURY

FY 1993	87
FY 1992	82
FY 1991	90

09/01/93-08/31/94

Objective: To determine the aqueous-phase free-radical chemistry, where we currently have only a threshold understanding.

Product: Additional scientific understanding of the general area of aqueous-phase chemistry.

Approach: The occurrence and behavior of aqueous-phase peroxides and their free-radical and ionic precursors (HO, HO₂, and O²⁻) will be investigated. A newly developed method for determination of hydrogen peroxide will be field tested and applied to the analysis of samples for hydrogen peroxide and organic peroxides. Low-intensity ⁶⁰Co gamma radiation will be employed to generate radicals representative of ambient concentrations to determine reaction rates and mechanisms associated with peroxide formation.

Results to Date: The fluorescence-based peroxide analyzer was deployed on three field missions this year. Different analytical conditions employed in the three-channel instrument allowed continuous measurement of hydrogen peroxide, hydroxymethyl hydroperoxide, and methyl hydroperoxide. Pumping scrubbing reagent to a glass coil mounted outdoors, where gaseous peroxides were absorbed directly, eliminated the potential for peroxide decomposition on the surface of inlet tubing.

Gas-phase peroxides were measured at a surface site in rural Georgia as part of the Southern Oxidant Study (SOS). Total peroxide concentrations ranged from the detection limit (0.2 ppbv) to 6 ppbv, with a mean daily high concentration around 2 ppbv, and hydrogen peroxide concentrations generally dominated.

We were one of three groups monitoring peroxides during the summer intensive of the SOS at Georgia Tech in Atlanta. Ozone concentrations were generally high, exceeding the 120-ppbv federal standard on several days. Total peroxides varied from the detection limit to approximately 6 ppbv, with a daily mean high concentration of 3.5 ppbv; and organic peroxides made up a significant fraction of the total on several days.

A year-long field program to examine seasonal trends in the concentration of peroxides, along with a limited set of auxiliary measurements (SO₂, O₃, and meteorological data) at Brookhaven National Laboratory (BNL), is currently in progress. Measurements made during the colder months disclosed the need for temperature control for accurate measurement in the Fenton channels; the system now includes this modification.

CONTINENTAL DRY AIR-SURFACE EXCHANGE

WESELY, M. L., and DOSKEY, P. V.

ARGONNE NATIONAL LABORATORY

FY 1993	175
FY 1992	175
FY 1991	175

10/01/92-09/30/93

Objective: To evaluate the exchange of trace chemicals in dry form between the atmosphere and natural surfaces in continental areas.

Product: An estimate of the role of dry deposition in the mass budgets of energy-related substances over North America.

Approach: This project will consist of field measurements, theoretical studies, and parameterization of dry-air-surface exchange rates. The results will be applied to estimate dry deposition at specifically designed network measurement stations with site-specific models and over large areas with regional- and global-scale models. For specific sites, an inferential technique will be used to compute weekly amounts of the dry deposition of sulfur dioxide, nitric acid vapor, sulfate and nitrate in fine particles, and ozone. The inferential approach will be used because existing reliable techniques to measure dry deposition directly are too complex for routine, continuous implementation, and the inferential approach requires data only on local meteorological and surface conditions and mean concentrations of the substances of interest. For regional- and global-scale models, a computer-coded module will provide estimates of the dry-deposition velocities for several selected inorganic and organic substances. Experimental and theoretical work will be conducted on measurement of air-surface exchange of organic substances, in addition to inorganic sulfur and nitrogen compounds and ozone because some organic substances are important in the tropospheric chemistry of energy-related trace substances. Processes of both emission and deposition of selected organic substances will be described mathematically in a form suitable for use in large-scale numerical models.

Results to Date: Field research centered on the use of environmental chambers to evaluate the emission and

uptake of nonmethane hydrocarbons by mixed grasses and broadleaf vegetation. Preliminary results indicate that the peak in emissions of total nonmethane hydrocarbons occurred during the period of most vigorous vegetative growth but that alcohols can be emitted during periods of high soil-moisture stress. Improvements in the basic techniques to model dry deposition over large areas were investigated by the use of remote-sensing data from satellites and by numerical modeling of chemical reactions that occur in the lower PBL. Estimates of surface resistance to the uptake of SO₂ and ozone over large areas were improved by use of surface-reflectance data from satellites and the combined modeling of the surface optical characteristics, turbulence inside canopies, and physiological processes of vegetation. Data from past micrometeorological experiments by ANL indicated good agreement with model predictions. To estimate the dry-surface removal of NO₂ with large-scale models, a combined second-order turbulence and chemistry model showed that NO₂ dry deposition can be underestimated if near-surface, rapid chemical reactions are ignored.

ATMOSPHERIC CHEMICALS' SOURCES AND FATES

WESELY, M. L., and SHANNON, J. D.

ARGONNE NATIONAL LABORATORY

FY 1993	200
FY 1992	200
FY 1991	200

10/01/92-09/30/93

Objective: To evaluate the fate of energy-related trace chemicals in the atmosphere in relation to their sources, chemical transformations, and processes of removal.

Product: Improved descriptions of potential changes of tropospheric pollutants, greenhouse-gas concentrations, and the tropospheric chemicals that affect the persistence and radiative properties of clouds.

Approach: Research will emphasize the assembly and analysis of data to construct mass budgets of nitrogen and sulfur species over North America and surrounding ocean areas. Data will be assembled and analyzed to integrate large-scale deposition fields in relation to both anthropogenic and natural emissions and estimation of off-continent transport. Collaboration with other par-

ticipants in the ACP involves measurements with aircraft and large-scale numerical modeling. In the collaborative research, efforts by ANL centers on evaluation of air-surface-exchange measurement techniques and on parameterization of the air-sea exchange of gases.

Results to Date: Theoretical and field studies were conducted on the air-sea exchange of energy-related gases. Parameterizations of resistance to vertical transport in the air and water sublayers in contact with each other at the interface were reviewed, and a refined model was produced. It will be incorporated into a dry-deposition computer-program module suitable for incorporation into large-scale atmospheric numerical models

on the fate of trace chemicals. Analysis of the data collected in FY 1992 during NARE continued satisfactorily and focused on evaluation of the performance of the eddy-flux measuring system aboard the G-1 aircraft. Collaboration continued with BNL on the use of ANL's dry-deposition module to compute large-scale estimates of the fate of SO_2 in North America. Significant transport of SO_2 from the North American continent to the North Atlantic is indicated in both the aircraft and the modeling studies. Theoretical studies continued on the fixation of nitrogen oxides by lightning, and estimates continue to support the assertion that natural production of NO_2 is considerably larger than currently inferred by many investigators.

ATMOSPHERIC DYNAMICS

The atmospheric-dynamics research supports the Division goals to:

- ▶ Improve the understanding of the emissions and processes that could potentially change global climate and
- ▶ Improve the understanding of the transport, dispersion, and chemistry of energy-related air pollutants.

The primary dynamics research component, Atmospheric Studies in Complex Terrain (ASCOT), is a multilaboratory program investigating mesoscale processes in the atmosphere by field experiments, mathematical modeling, and theoretical research.

Research Objectives. ASCOT's objectives are to:

- ▶ Improve fundamental knowledge of the atmospheric dynamics and air-pollution-dispersion processes in complex terrain,
- ▶ Incorporate this knowledge in the development of tools for air-quality assessments, and
- ▶ Apply these tools to atmospheric-dispersion problems associated with emergency response to the release of hazardous materials.

Research Questions: Differential heating and cooling of the boundary layer over variously exposed surfaces drive local and regional circulations that change unpredictably throughout the day and night. These circulations interact with or are protected from the overlying synoptic wind fields, depending on terrain and meteorological conditions. The description and forecasting of these evolving complex flow patterns and the dispersion of contaminants released within them are highly

uncertain and constitute the current scientific focus within the ASCOT program.

A balance is maintained in ASCOT between a primary focus on basic science and a relevance to DOE mission needs. The central scientific emphasis on evolving energy transfers in flow-field development, terrain influences on mechanical and thermal forcing, and the scale interactions between circulations from local to synoptic scales must be pursued with the intent of ultimately serving the long-term needs of DOE and the country. The program maintains an awareness of needs in emergency preparedness, energy-related-air-pollution concerns, and climate-change studies and modeling. Transfer of the research findings of ASCOT to elements of DOE and other agencies directly involved in solving operational and policy-related problems is an active part of the planning and program activities within ASCOT.

During the past few years, ASCOT has focused its research on areas in which DOE facilities are located (i.e., in the Tennessee Valley near Oak Ridge and in Colorado's Front Range region near the Rocky Flats Plant). Studies of the flow patterns in the Tennessee Valley have examined the relationship of local valley winds to large-scale wind patterns and have investigated methods of characterizing the spatial variability of the winds with a limited number of observation sites. Such studies are relevant to the prediction of plume transport and diffusion in areas of complex terrain and should be useful in emergency-preparedness applications.

In the Front Range, ASCOT participated in a meteorological and tracer experiment in the winter of 1991 and has been assessing the role that drainage winds from the slopes and valleys of the mountains

play in the dispersion of material that might be released from the Plant in the unlikely event of an accident. ASCOT has also recently completed a three-month measurement program during the summer and fall of 1993 in the Front Range area that employed an array of remote sensors to obtain wind and temperature profiles over the mountains, the adjacent plains, and the mouth of a canyon to the northwest of the Plant. The data will be used to study the interaction of regional and local flows and their impact on the local meteorology of the Rocky Flats Plant.

Future studies will include further extended-measurement campaigns that use remote-sensor technology (supplemented with shorter, intensive campaigns with additional instrumentation) to study selected features of the meteorology in the Front Range area. The possibility of carrying out additional tracer studies will be pursued. This work, along with continuing studies in the Tennessee Valley, will be directed toward improved descriptions and predictions of the structure and

evolution of the atmospheric boundary layer, the effects of complex topography on that structure, and the implications for the transport and diffusion of atmospheric pollutants released in such regions.

Program Manager

Michael R. Riches
Environmental Sciences Division
ER-74
Department of Energy
Washington, DC 20585
301-353-3264

Principal Scientist

J. Christopher Doran
Atmospheric Sciences Department
Pacific Northwest Laboratory
P.O. Box 999
Richland, WA 99352
509-376-4734

Research Summaries

ATMOSPHERIC TRANSPORT OF CONTAMINANTS

ADDIS, ROBERT P.

WESTINGHOUSE SAVANNAH RIVER COMPANY

FY 1993	200
FY 1992	200
FY 1991	200

10/01/92-09/30/93

Objective: To evaluate and improve mesoscale modeling of atmospheric flow and contaminant transport for emergency-response applications.

Product: An understanding of the limitations and improvement in the capabilities of mesoscale atmospheric transport models in emergency-response applications.

Approach: The applicability of mesoscale atmospheric models in emergency response depends on the accuracy of contaminant-transport prediction, operational functionality, reliability, and computational speed. This project will evaluate the meteorological and transport predictions made by the Colorado State University (CSU) mesoscale Regional Atmospheric Modeling System (RAMS) and a Lagrangian particle dispersion model (LPDM). These models will be used to calculate the wind field and contaminant transport at both Rocky Flats and the Savannah River Site (SRS). The modeling studies at Rocky Flats will be performed in conjunction with the ASCOT 1992 winter field experiments. Model results will be compared with meteorological and tracer data from both sites. These results will also be compared with the predictions of several diagnostic models. The accuracy of model predictions and computational requirements will be evaluated as functions of model grid size, grid nesting, parameterizations, and boundary conditions.

Results to Date: The atmosphere over the front range of the Colorado Rocky Mountains was simulated with the CSU RAMS. Simulations were performed with an additional high-resolution nested grid (330 m). This grid

was centered over Rocky Flats, allowing a much better resolution of the jets exiting Eldorado and Coal Creek canyons. The impact of these jets at Rocky Flats was investigated. 2-D simulations of slope flows suggested that the deformation-based turbulence scheme in RAMS might not be producing adequate results. Thus, a second-order turbulence parameterization was added to the RAMS model for the simulations. Sensitivity studies were then performed to evaluate the effect of turbulent length scale, roughness heterogeneity, and radiation parameterization on the thermal structure of the Platte River drainage. The 4-D data-assimilation technique (4DDA) previously incorporated in RAMS was also used to simulate wind fields on the high-resolution grid. The results compared with those without 4DDA. The particle model used with RAMS for transport calculations was modified to take advantage of the second-order moments computed in the new turbulence parameterization. Tracer releases from Rocky Flats were simulated with the high-resolution grid and the modified particle model. The results were compared with previous plume calculations.

To gain a more fundamental understanding of terrain-induced flows, 3-D simulations over idealized valley-plain-tributary systems were performed. At issue here is the effect of tributaries on the flow behavior of a plain-valley system. To understand the effect of unresolved terrain, 2-D simulations of east-west cross-sections over the Rockies were performed with both high (1-km) and low (10-km) terrain resolution. These studies represent an initial look at the effect of terrain resolution on surface parameterizations and the nesting scheme used in RAMS.

ATMOSPHERIC DIFFUSION IN COMPLEX TERRAIN

ALLWINE, K. JERRY

PACIFIC NORTHWEST LABORATORY

FY 1993	174
FY 1992	174
FY 1991	148

10/01/92-09/30/93

Objective: To identify the forcing mechanisms responsible for observed wind and temperature structures in complex terrain and to develop, test, and apply numerical models that describe these mechanisms and their effects on the transport and dispersion of atmospheric pollutants.

Product: An understanding of the physical processes governing the transport and diffusion of atmospheric pollutants in complex terrain and the description of these processes with appropriate numerical or conceptual models.

Approach: Field data and numerical-modeling results will be used to identify mechanisms responsible for the development and structure of wind and temperature fields in regions of complex terrain. The field and numerical-simulation results will be integrated to develop and test the ability to describe and predict wind and temperature structure and the behavior of pollutants in such environments. Numerical models will be refined and optimized to produce efficient, accurate, and reliable codes for research and application needs.

Results to Date: The experimental and theoretical bases of nighttime diffusion and daytime ventilation of pollutants from a deep mountain valley have been established. Stagnation, ventilation, and recirculation have been mathematically defined so they can be used to describe the air-pollution characteristics of various airsheds. The dominant meteorological processes governing the nighttime near-surface dispersion in the vicinity of Rocky Flats have been identified. A nested version of a diagnostic flow model has been described that is applicable in complex terrain used in the PGEMS emergency-response dispersion model.

The results from the PGEMS dispersion model have been compared with the 1991 Rocky Flats tracer data to test the validity of the modeling approach. Sigma-theta data from the Grand Canyon region are being analyzed to determine the relationship of sigma-theta with land-form type. Additionally, a numerical method is being formalized and tested for determining the soil heat flux from soil-temperature-profile data.

ATMOSPHERIC BOUNDARY LAYER TRANSPORT AND DISPERSION STUDIES

COULTER, R. L., and WESELY, M. L.

ARGONNE NATIONAL LABORATORY

FY 1993	175
FY 1992	175
FY 1991	175

10/01/92-09/30/93

Objective: To examine the nature of atmospheric flow over complex terrain, particularly over sites where the future construction of power-production or fuel-conversion facilities is being planned and where the potential exists for release of toxic materials to the atmosphere, so that improved estimates can be made of the rates at which airborne pollutants are diluted, removed by dry and wet processes, and delivered to sensitive receptors.

Product: Improved air-pollution and emergency-response models that are required to plan and manage energy-generation and fuel-conversion facilities.

Approach: To study transport over complex and nonuniform terrain, this research group will participate in large, multiorganizational field experiments.

Experimental studies will be conducted with remote-sensing equipment, such as Doppler acoustic sounders and laser anemometers, and with direct-sensing devices deployed at the surface or carried aloft by free or tethered balloons. Advanced acoustic sounder systems will allow evaluation of the vertical structure of the mean and turbulent, 3-D wind components in the lower atmosphere without the use of instruments in towers. Transport and diffusion processes will be described mathematically, and these descriptions will be tested against experimental data.

Results to Date: Data from the 1991 field study around the Rocky Flats Plant in the Front Range of the Rocky Mountains have been analyzed. Analysis of the outflow from Coal Creek Canyon at several locations on Feb. 4-5 and 6-7, 1991, was compared with an analytical model of flow dispersion from the canyon as the flow spread over the plains toward the Rocky Flats Plant. The model assumes an exponential decrease in the downstream-plume wind speed; that is, the rate of

decrease of the wind speed is proportional to the speed itself. Minisodar data from the mouth of Coal Creek and three sites downstream along with tower windspeed and direction from the Rocky Flats Plant gave good agreement between the model-predicted plume depth and speed downstream from Coal Creek. Further enhancements of the model include conservation of momentum within the plume.

The statistical results have been compiled from almost 2 years of continuous operation of the data network in the Front Range area, including the eight-tower and two-minisodar network. The occurrence of well-defined drainage flow from Coal Creek correlated well with the net radiation and near-surface winds at towers located in the drainage region of the valley.

The central hub for the ASCOT data network was established with a computer system borrowed until the computer purchased by ASCOT arrives. Data are being archived from the network as well as from the PROFs network and the Rocky Flats Plant tower. Data from the Rocky Flats Plant tower since October 1990 has been made available on the hub. Data from the extended network will be available on the hub over the Internet.

ASCOT PROGRAM SCIENTIFIC DIRECTION

DORAN, J. CHRISTOPHER

PACIFIC NORTHWEST LABORATORY

FY 1993	165
FY 1992	165
FY 1991	155

10/01/92-09/30/93

Objective: To provide scientific coordination among the primary DOE laboratories participating in the Atmospheric Studies in Complex Terrain (ASCOT) program and with supporting NOAA laboratories and university groups.

Product: Focused, common objectives and complementary approaches to the individual research of the contributing scientists from the primary laboratories and supporting research groups.

Approach: A scientific focus will be defined for the program, representing the consolidated interests of the

participants and some of the most urgent challenges to the scientific community and at the same time identifying and linking DOE's mission-related needs with the scientific outputs. Emphasis will be directed toward providing results important to emergency-response needs. The project will maintain this focus for ASCOT through planning with representatives of the participating laboratories, strengthening the organizational components of the program, promoting collaboration and exchange among the scientists involved, enhancing direct and frequent communications with participants and with DOE, and promoting technology transfer to user groups within DOE and elsewhere.

Results to Date: A workshop was organized for ASCOT participants in February 1992 in Salt Lake City, Utah. Participants presented results of their work in a variety of areas, with an emphasis on dispersion along Colorado's Front Range near the Rocky Flats Plant. Extensive discussions on an experiment planned for the summer and fall of 1993 were also held. A Science Oversight Group, composed of scientists from universities and industry, attended the workshop and provided feedback on the workshop activities and the program's direction. Funding was provided to NOAA's Wave Propagation Laboratory to install and operate two radar profilers in the South Boulder Creek drainage area as part of the summer experiment. A request for proposals was developed for funding of ASCOT research for FY 1995-1997. Following one of the suggestions of the Science Oversight Group at the February meeting, planning began for a modelers' workshop.

DIRECT SIMULATION OF ATMOSPHERIC TURBULENCE

DORAN, J. CHRISTOPHER

PACIFIC NORTHWEST LABORATORY

FY 1993	250
FY 1992	250
FY 1991	140

10/01/92-09/30/93

Objective: To simulate the dynamics and turbulent properties of the planetary boundary layer (PBL) in an effort to identify and characterize the dominant mechanisms that determine the behavior of the PBL.

Product: Increased understanding of geophysical fluid turbulence and the structure and characteristics of the PBL, particularly in regions of complex terrain, and improved predictive capability for the description of transport and mixing in turbulent atmospheric layers.

Approach: Advanced computational models will be used to study the effects of nonlinear dynamics and turbulence on the properties of the PBL in complex terrain. Models will be used to describe the mean and turbulent motions responsible for PBL characteristics. New and improved models of turbulence in stably stratified layers will be developed, and improved parameterization schemes will be incorporated for processes like turbulent exchange and surface energy balances in existing mesoscale models.

- ▶ One or more numerical mesoscale models will be applied to simulate the structure and evolution of the PBL in areas of interest to DOE missions. Numerical experiments will be carried out to identify the primary physical mechanisms responsible for unusual or anomalous features of local and regional circulations and atmospheric stratification.
- ▶ The properties of the PBL will be related to the behavior of atmospheric pollutants released into the environment and compared with observations where possible.
- ▶ Through collaboration with the university researchers, a full-turbulence simulation (FTS) model of flows over an inclined surface in stably stratified flows will be developed.
- ▶ The results of the FTS model will be applied to a search for improved representation of turbulence in stable layers in mesoscale models, incorporating features such as wave-turbulence interactions.
- ▶ Modules will be developed and incorporated that improve the representation of turbulent exchange and other physical mechanisms in available numerical models.

Results to Date: In a cooperative effort with the Coupling and Decoupling of Atmospheric Circulations project, a modeling and data-analysis study of the interactions of ambient and valley winds in the Tennessee Valley was completed. A study of regional drainage winds in the Pacific Northwest was also carried out. The mechanism for the development of the

moderately strong winds that regularly develop around sunset in the Hanford area during the spring and fall was identified. A series of sensitivity experiments provided additional insight into the topographic and thermal forcing that causes these flows. Support was provided toward the deployment of two sodars and a radar profiler with RASS to be used in a summer and fall observational program in the Front Range near the Rocky Flats Plant. Data obtained in this study will provide the basis for supplementary numerical simulations of scale interactions in this area. Support for a graduate research program in the application of full-turbulence simulations to the study of stable boundary layers over a sloping surface was continued.

SUPPORT FOR COMPLEX-TERRAIN STUDIES

GUDIKSEN, PAUL H.

LAWRENCE LIVERMORE NATIONAL LABORATORY

FY 1993	313
FY 1992	313
FY 1991	313

10/01/92-09/30/93

Objective: To measure meteorological variables in support of the Atmospheric Studies in Complex Terrain (ASCOT) Program and to develop and evaluate numerical models that are capable of faithfully simulating the physical processes responsible for pollutant dispersion in areas of complex terrain.

Product: Evaluated models of pollutant dispersion processes associated with terrain-dominated flows.

Approach: Our meteorological studies in western Colorado that involve investigating the effects of the ambient meteorology on the wind and temperature characteristics of nocturnal drainage flows in a mountain valley will be completed. Assistance will be provided in the transfer of the ASCOT field studies program to the Rocky Flats area. A network of meteorological towers will be installed and operated to support climatological studies in the Rocky Flats area. Climatological data will be analyzed to define the frequency of occurrence of nocturnal drainage flows in the Rocky Flats area and to define their temporal and spatial wind and temperature characteristics. Diagnostic model simulations will be performed on the winter 1991 tracer experiments.

ASCOT data and results of our model simulations will be exchanged with Rocky Flats personnel to assist their emergency-preparedness program.

The field measurements, data analysis, and model applications and support provided by this task will be closely integrated with the ASCOT model development activities to ensure that the field data acquired are useful for understanding the physics of the terrain-dominated flows under study as well as to provide the data needed for model-validation efforts. These activities have been well coordinated with other ASCOT program participants.

Results to Date: Investigations of the drainage flows within the Coal Creek Canyon near the Rocky Flats Plant revealed that the net radiative cooling along the valley slopes and the strength of the ambient flows above the valley controlled drainage-flow development. A net radiative-cooling rate exceeding 50 W/m^2 produced a strong drainage flow of about 125 m in depth and a well defined 6 m/s jet at a height of 60 m. Cooling rates of less than 30 W/m^2 produced weak drainage flows characterized by a uniform vertical wind structure of about 2 m/s. No observable drainage flows occurred below 15 W/m^2 . Ambient flows above the valley exceeding 5 m/s tended to destroy any drainage-flow development.

A stochastic diffusion module based on the 3-D Langevin equation was incorporated into the ADPIC dispersion model. Simulations of the Rocky Flats Winter 1991 tracer experiments indicated that this more fundamental method produced closer agreement between model predictions and observations than that derived from the present gradient approach.

Our technical-transfer activities were focused on organizing an emergency-response meeting in Germany that was sponsored by the Commission of European Communities (CEC) and DOE and a conference in the United States on environmental transport and dosimetry that was sponsored by the American Nuclear Society.

ATMOSPHERIC TURBULENCE AND DIFFUSION RESEARCH

HOSKER, R. P., JR.

ATMOSPHERIC TURBULENCE AND DIFFUSION DIVISION, NOAA

FY 1993	250
FY 1992	250
FY 1991	250

10/01/92-09/30/93

Objective: To (1) develop better methods of describing atmospheric transport, diffusion, and air-surface exchange (including deposition) in numerical simulations; (2) extend the applicability of these techniques to realistic situations, such as nonstationary conditions, complex terrain, and dense vegetation; and (3) develop and test improved numerical models incorporating these new methods.

Product: The development of predictive capabilities that use the results of this research.

Approach: Dispersion and planetary boundary layer studies (C. J. Nappo, Jr.) will extend contemporary understanding of transport and dispersion in the lower atmosphere to nonideal conditions and will provide improved methods for measuring atmospheric-plume dispersion rates and for including realistic dispersion parameters in numerical models. Activities will focus on the roles of wave/turbulence interaction and sporadic nocturnal turbulence as mechanisms for accelerating dispersion at night and on the consequences of releases of dense and/or chemically reactive pollutants.

The research on canopy micrometeorology (D. D. Baldocchi) will identify and quantify the interactions involved in above- and within-canopy transport, dispersion, and deposition in canopy-atmosphere exchanges of materials and energy. Such information will be used to include and/or parameterize physical and biological surface effects in numerical models ranging from local to global scales.

Air-surface exchange of trace gases and aerosols will be studied with eddy-correlation techniques (D. R. Matt). Direct measurements of deposition fluxes together with ancillary physical-biological characterization of the surface will provide reference data for parameterization

of the exchange processes. These studies will provide benchmark data for inferential measurement method development and testing.

Physical modeling (R. P. Hosker) will be used to complement contemporary mathematical models of plume dispersion that are not adequate to calculate concentrations of pollutants when the plume is affected by hills and buildings. Small scale models will be immersed in the flow of a wind tunnel to simulate transport and diffusion in a timely and relatively inexpensive manner. A wind tunnel is available for modeling studies in conjunction with other ATDD programs.

Results to Date: A program was developed to calculate statistical performance measures of air-quality models. Data from a Boardman, Oregon, DOE-ARM study are being used to study intermittent episodes of turbulence in the stable PBL. Higher-order-closure PBL models and a 2-D Lagrangian particle-dispersion model were adapted for "footprint" analyses of scalar flux measurements over nonhomogeneous surfaces. A collaboration was begun with Uppsala University to parameterize upper-PBL turbulence generation caused by breaking gravity waves; a field study of turbulence structure is being jointly planned. An analytical model to calculate leaf processes was developed from current theory, tested, and incorporated into a model to predict exchanges of heat, water vapor, CO₂, and isoprene over forests and crops; the model has excellent potential for improving current schemes to estimate exchanges of SO₂ and O₃. A seasonal study of CO₂ and water-vapor exchanges over a forest is under way. Planned flux measurements of water vapor, SO₂, and CO₂ in eastern Germany will be used to test air-surface-transfer parameterizations for sulfur in the dry-deposition inferential method. A wind-tunnel study of flow across parallel ridges at an angle to the approaching wind was performed.

COMPLEX TOPOGRAPHY (ASCOT)

HOSKER, R. P., JR.

ATMOSPHERIC TURBULENCE AND DIFFUSION DIVISION, NOAA

FY 1993	297
FY 1992	297
FY 1991	297

10/01/92-09/30/93

Objective: (1) To design, plan, and conduct with other participating ASCOT laboratories, field experiments investigating mesoscale circulations in areas of complex terrain and the dispersion of contaminants released within them; (2) to analyze meteorological and turbulence data and tracer concentrations measured in ASCOT experiments to improve understanding of the characteristics of flow and dispersion in complex terrain; and (3) to develop and evaluate numerical models of flow and dispersion in drainage flows in complex terrain.

Product: Databases characterizing complex airflow and dispersion over nonuniform terrain under varying conditions of thermal and mechanical forcing and influences of multiscale interactions among local, regional, and synoptic flow fields; useful physical concepts and hypotheses that have been tested with these databases; and validated numerical models of flow and dispersion in complex terrain that can be used for research, parameterization studies, safety and risk assessment, and regulatory applications.

Approach: Meteorological measurements will be made to characterize mesoscale circulations and the fluxes that determine their evolution. Sodar, tether sondes, airsondes, and other sounding instrumentation will be used to provide periodic profiles of wind speed and direction, temperature, humidity, turbulence, and certain trace gases. Tower networks will continuously detect near-surface variables and gradients that, together with turbulent flux instrumentation and radiometers, provide surface energy budgets and other exchanges between atmosphere and surface as well as their spatial and temporal variabilities. Flux and turbulence measurements from low-flying light aircraft will also provide both horizontal and vertical variations important to scale-interaction studies and evaluations of flux divergences and wave generation.

Concentration and meteorological data will be edited and analyzed to provide information to execute numerical models and to test them. The data analyses will be explained in terms of tracer release height, topography, winds, synoptic conditions, etc.

Transport and dispersion models suitable for use in complex terrain will be developed and tested with the data sets. A variety of statistical techniques will be applied to quantify the ability of the models to predict winds, turbulence characteristics, and/or concentrations, as appropriate.

Results to Date: Data from the Rocky Flats Plant study were analyzed, and hourly tracer-concentration values were simulated. A 2-D stochastic dispersion model (LSDM) was developed and tested with data from the Geysers study; it is used with ATDD's katabatic-flow model for parameterization studies. A 3-D version of LSDM is being tested with tracer data from the Brush Creek and Rocky Flats studies. A climatology and analysis of surface atmospheric-pressure perturbations was begun; a survey of vertical structure of windspeed and temperature over Oak Ridge is under way. Analysis of the stable PBL over complex terrain continued with data from the Oak Ridge study. A high-resolution transport and diffusion model for complex terrain is being developed for Oak Ridge.

TERRAIN-INFLUENCED METEOROLOGY

LEE, J. T., and BOSSERT, JAMES

LOS ALAMOS NATIONAL LABORATORY

FY 1993	560
FY 1992	560
FY 1991	560

10/01/92-09/30/93

Objective: To develop and verify improved estimation techniques for atmospheric transport and diffusion in sites of generalized topography.

Product: A fundamental understanding of atmospheric transport and diffusion in sites of generalized topography leading to improved models for atmospheric transport and diffusion calculations.

Approach: The terrain-influenced meteorology program will be formulated in a balanced approach among field experiments, laboratory simulations, and numerical modeling. The physics is vital in identifying important phenomena to be measured and modeled and in interpreting the results of the experiments. The approach will place an emphasis on the fundamentals of transport and diffusion in complex terrain. In practice, field measurements will be emphasized with the primary thrust in intensive experiments designed around clearly defined objectives. A high ratio of interpretation effort to data gathering will be maintained to explore as fully as possible the important phenomena governing the transport and dispersion at a particular site. The models that are implemented will have a similar emphasis on identifying

and qualifying important complex-terrain phenomena. Once an understanding is achieved of the processes governing the transport in terrain-dominated airflow and its relation to general meteorological conditions, the parameterization of these processes for incorporation into operational air quality models will be more systematic and reliable.

To simulate pollutant diffusion and transport over complex terrain, accurate estimates must be made of the spatial distribution and temporal development of winds and turbulence. A 3-D mesoscale numerical model has demonstrated considerable ability to simulate geophysical fluid flows under quite general boundary conditions. The model equations are time dependent and three-dimensional in space so that temporal and spatial variations of temperature stratification are included. The model has been applied to obtain predictions of mesoscale wind fields for various large-scale weather conditions.

Results to Date: Analysis of the meteorological data collected during the 1991 Front Range field study in the vicinity of DOE's Rocky Flats Plant and the atmospheric tracer data from the Rocky Flats Winter Validation Study has continued during FY 1993. The four nighttime tracer-release experiments have been simulated with the RAMS/LPDM prognostic wind field and dispersion models and the ATMOS 1/2 diagnostic wind-field and dispersion models. Results from both codes are encouraging, with peak concentrations typically accurate to within $\pm 50\%$ and the location of the peak concentration on the sampler arc to within ± 45 degrees. Additional simulations and detailed comparisons of the prognostic and diagnostic model results are in progress as well as simulations of the daytime and transition tracer experiments.

During FY 1993 we have maintained and distributed the database from the ASCOT 91 field experiment and have continued the plotting, archiving, and distribution of data from the LLNL tower network in the Rocky Flats area.

We participated in the ASCOT 93 Front Range field experiment by deploying a minisodar to study the drainage flow from El Dorado Canyon, two meteorological stations on mountain peaks at Elk Mountain and Steamboat Springs to provide supporting data for the profiler measurements across the continental divide, and laser anemometers to study drainage flows in an area northwest of the Rocky Flats Plant.

MESOSCALE EMERGENCY RESPONSE

LEONE, J. M., and GUDIKSEN, P. H.

LAWRENCE LIVERMORE NATIONAL LABORATORY

FY 1993	300
FY 1992	300
FY 1991	400

10/01/92-09/30/93

Objective: To develop and evaluate the LLNL diagnostic and finite-element-based dynamic models of the atmosphere to improve and enhance their ability to simulate flow and dispersion over complex terrain.

Product: Evaluated models of pollutant-dispersion processes associated with terrain-dominated flows.

Approach: The diffusion module will be improved in the MATHEW/ADPIC diagnostic models that currently form the core of the Atmospheric Release Advisory Capability (ARAC) emergency-response service. The initialization and turbulence-parameterization schemes will be improved in the finite-element-based boundary-layer models. FEM-PBL, the nonhydrostatic model, will be applied within the ASCOT experimental areas for improving the understanding of valley circulations. Development of SABLE, a hydrostatic mesoscale boundary-layer model that is expected to be suitable for emergency-response calculations, will be continued. The ADPIC model will be coupled with SABLE for subsequent inclusion in the ARAC service.

Because the ASCOT program is currently focusing its research resources on problems associated with DOE's emergency-preparedness responsibilities, the plan is to continue these model-development efforts and to augment them with the development of a hydrostatic-boundary-layer model that may be suitable for emergency-response forecasting. This development effort will also provide the framework needed to define the conditions under which the simpler hydrostatic assumption may be adequate for describing the dispersion processes.

Results to Date: The second Rocky Flats 1991 dispersion experiment was simulated with the SABLE/ADPIC model suite. This code combination reproduced many of the experiment observations. Although the simulated

plume was late arriving at the second sensor arc, by the second hour, the agreement between the simulated plume and the observations was significant. The simulation continued to show skill until hour eight, when the simulated plume drifted too far south. This southerly drift continued through the last 4 h of the simulation, and by hour 10 the simulation had no relation to the observed plume. The cause of this error was traced to the development of a 2-m/s-larger-scale wind during the experiment that was not simulated because of the lack of the larger-scale forcing.

We have also been using SABLE to simulate idealized flow development in the Coal Creek Canyon area, where we have long-term observations. The observations suggested a strong relationship between surface heat flux and the magnitude and shape of the drainage wind out of the canyon. We have reinforced this relationship by noting a similar relationship in our numerical simulations.

INTERACTIONS BETWEEN SURFACE EXCHANGE PROCESSES AND ATMOSPHERIC CIRCULATIONS

SHAW, WILLIAM J.

PACIFIC NORTHWEST LABORATORY

FY 1993	150
FY 1992	150
FY 1991	45

10/01/92-09/30/93

Objective: (1) To evaluate systematically, through the use of advanced numerical models, the effects of variable surface fluxes of heat, momentum, and moisture over heterogeneous surfaces on the local and regional circulations in the planetary boundary layer; (2) to establish techniques for measuring and describing appropriate, representative values of these fluxes for use in parametric representations of their effects; (3) to examine possible feedbacks that boundary-layer properties may have on the surface characteristics; and (4) to study the diurnal and seasonal variability in these processes.

Product: An improved understanding of the interactions among surface fluxes of heat, momentum, and moisture and the characteristics of the atmospheric boundary layer.

Approach: Improved models for describing air-surface exchanges of momentum and sensible and latent heat will be acquired or developed, and these descriptions will be incorporated in existing mesoscale computer codes. Latent and sensible heat fluxes over semiarid terrain will be measured. This task will examine questions of measurement techniques; representativeness of flux values; and the use of observed, interpolated, and extrapolated fluxes as boundary conditions for mesoscale models.

Results to Date: Observations of surface fluxes and related variables made during the transition period from active growth to senescence for the annual grasses in the Northwestern shrub-steppe region were analyzed to develop improved subgrid-scale parameterizations for heterogeneous surface conditions in global climate models. Evaluation of surface exchange modules used in regional and larger-scale models with this data set is continuing.

A 915-MHz wind profiler with a radio acoustic sounding system (RASS) was installed and evaluated. The profiler is an outstanding addition to the observational resources for this program. Direct comparisons of winds and temperatures with the 122-m tower at the Hanford Meteorological Station (HMS) shows that the hourly averages of winds agree between the two systems to within 1 m/s in each component and that the hourly averages of temperature agree to within 0.5°C. A data-processing scheme is being tested that would produce profiles of turbulent momentum flux from the profiler. Momentum-flux measurements made for several weeks in May 1993 with acoustic anemometers mounted on the HMS tower are being compared with profiler-derived fluxes. If successful, this technique holds the possibility of doing single-station evaluations of the heat balance.

COUPLING/DECOUPLING OF LOCAL AND SYNOPTIC CIRCULATIONS

WHITEMAN, C. DAVID

PACIFIC NORTHWEST LABORATORY

FY 1993	224
FY 1992	224
FY 1991	186

10/01/92-09/30/93

Objective: To develop an improved understanding of physical mechanisms leading to interactions between thermally driven, local wind systems and the ambient flows.

Product: Improved atmospheric transport and diffusion models capable of predictions in complex terrain for use in emergency response and environmental assessment.

Approach: A better understanding will be gained of the basic physics, the driving forces, and the interactions of thermally developed complex-terrain circulations of different scales. These complicated interactions represent significant challenges that will be met with an integrated program of new field investigations, data analysis from past complex-terrain experiments, and mathematical modeling of relevant physical mechanisms. Field investigations will make use of remote and in situ atmospheric-sounding devices, radiation- and energy-budget measurement systems, tracer samplers, and basic meteorological sensors. Data sets will come from ASCOT and other complex-terrain experiments, and simulations will come from a variety of meteorological models, from simple thermodynamic to full-physics numerical models.

Results to Date: A new method of identifying physical mechanisms responsible for synoptic and valley-flow coupling was developed that uses pattern recognition and wind-direction frequency distributions. This technique was illustrated for the Tennessee Valley and was supported by numerical simulations. A new technique was also developed for quantifying stagnations, recirculations, and ventilations, with applications to air-pollution dispersion. Further, a Monte Carlo technique was developed to calculate uncertainties in atmospheric heat budgets measured by triangular arrays of radar profilers and remote acoustic-sounding systems. Future ASCOT experiments will use these devices. Finally, new numerical simulations were begun to investigate thermally driven flows that develop between basins and plains. The project supported the deployment of meteorological equipment for a field experiment in Colorado's Front Range.

OZONE PROJECT

Over the past two decades, DOE ozone research has focused on the polluted regional troposphere. More recently, DOE ozone research efforts have expanded, in response to the National Energy Policy Act, to include the global free-troposphere and the midlatitude, lower stratosphere.

Research Objectives. The objectives of the DOE Ozone Project are to:

- ▶ Improve estimates of ozone and UV-B trends;
- ▶ Improve the understanding of the chemical and dynamic processes controlling ozone formation and destruction; and
- ▶ Develop improved predictions of future ozone concentrations and their climatic interactions.

These objectives follow from specific DOE information requirements [an identified subset of the research and evaluation needs delineated in the Intergovernmental Panel on Climate Change (IPCC), World Meteorological Organization (WMO), and United Nations Environment Programme (UNEP) science assessments], are being met by means of strong interaction with other federal agencies and international organizations, and are intended to maximize programmatic benefit to policy analysts.

Such activities include: (1) augmentation and quality assurance of ozone and UV-B monitoring

networks (particularly by the WMO Global Atmospheric Watch); (2) systematic reevaluation and interpretation of the historical ozone measurements; (3) specific research on chemical mechanisms for ozone formation and destruction (sensitivity/uncertainty evaluation of existing kinetics parameterizations and determination of previously undiscovered and unquantified mechanisms); (4) evaluations of the joint action of transport and chemistry in determining the state of midlatitude, lower-stratospheric ozone through global models and other diagnostic tools; and (5) advanced instrumentation development for lower stratospheric chemical measurements.

Program Manager

Michael R. Riches
Environmental Sciences Division
ER-74
Department of Energy,
Washington, DC 20585
301-903-3264

Principal Scientist

Jeremy M. Hales
Envair
4811 W. 18th Ave.
Kennewick, WA 99337
509-735-9480

Research Summaries

LABORATORY STUDIES OF THE SENSITIVITY OF TROPOSPHERIC OZONE TO THE CHEMISTRY OF SEA-SALT AEROSOL

FINLAYSON-PITTS, B. J.

CALIFORNIA STATE UNIVERSITY AT
FULLERTON

FY 1993	240
FY 1992	0
FY 1991	0

09/15/93-09/14/94

Objective: To examine sea salt as a possible significant source of tropospheric halogen (chlorine and bromine) radicals through heterogeneous reaction with nitrogen oxides.

Product: An improved understanding of sea salt and salts from alkaline volcanoes as sources of halogen radicals that may affect tropospheric and stratospheric ozone.

Approach: Knudsen-cell studies will investigate gas-solid reaction probabilities for reactions of NO_2 , N_2O_5 , ClONO_2 , and HNO_3 with NaCl and NaBr . Other potential reactions, such as HOCl with NaCl , will also be explored. This reaction is thought to be a significant intermediate step in the overall reaction of ClONO_2 , HCl , and ice and may be important in the troposphere as well as the stratosphere. In the experiments, the change in gaseous reactant when the gas is exposed to the solid will be measured. Fourier-transform infrared analysis and mass spectrometry (FTIR/MS) will be used to study the effects of temperature and light on the kinetics and the products when relative humidity is above the deliquescence point and the salt particle becomes a concentrated solution.

Rate studies of chlorine-atom reactions with biogenic hydrocarbons, such as isoprene, will be conducted under tropospheric conditions, and the relative rate will be compared with known rate constants of an organic, such as propene. The absolute rate constants for chlorine atoms with organics will be determined with a fast-flow discharge system with resonance-fluorescence detection of chlorine atoms. Mechanistic studies will be conducted

with the FTIR in a long-path White cell to understand the loss of organic and the formation of products with time in reactions with chlorine. Reactions of ClNO and ClNO_2 with gaseous water will be studied with the FTIR/MS. The kinetics will be obtained from the rate of reactant loss, and the products will be identified and quantified. The data obtained from these experiments will be used in a simple 0-D kinetic model to assess the contribution of sea-salt aerosols to the formation of chlorine and bromine atoms in the troposphere and their role in determining tropospheric ozone.

Results to Date: New project.

REEVALUATION OF TOTAL AND UMKEHR OZONE DATA FROM TEN NOAA/CMDL DOBSON SPECTROPHOTOMETER OBSERVATORIES

HOFMANN, DAVID J.

NOAA CLIMATE MONITORING AND
DIAGNOSTICS LABORATORY

FY 1993	73
FY 1992	0
FY 1991	0

09/15/93-09/14/94

Objective: To reevaluate total and Umkehr ozone data, including corrections for instrument calibration and instrument changes.

Product: An improved column ozone data set for research on global ozone trends and ozone and climate-change research.

Approach: NOAA has 377 station-years of total-ozone data and 57 station-years of Umkehr data obtained at 24 stations around the world. The total ozone data obtained by the Dobson spectrophotometers at four stations (Haute Provence, France; Lauder, New Zealand; Perth, Australia; and Poker Flat, Alaska) will be reevaluated. Umkehr data will also be evaluated from Boulder, Colorado, and Mauna Loa, Hawaii. The data from six Dobson stations (Fairbanks, Alaska; Huancayo, Peru; Puerto Montt, Chile; South Pole, Antarctica; Halley, Antarctica; and Byrd, Antarctica) and the Umkehr data

from Huancayo will then be reevaluated in accord with procedures described in the WMO *Dobson Spectrophotometer Data Reevaluation Procedures Handbook, Sect. II: Reevaluation of Instrument Constants*. The reevaluated data will be subjected to statistical analyses and checked for internal consistency to identify problem areas and to assess the representativeness of the statistically derived variables. The analyses and the reevaluated data will be archived and made available for use.

Results to Date: New project.

STATISTICAL ANALYSIS AND INTERPRETATION OF STRATOSPHERIC OZONE AND TEMPERATURE TRENDS WITH SATELLITE DATA

HOOD, LON L.

UNIVERSITY OF ARIZONA

FY 1993	88
FY 1992	0
FY 1991	0

09/15/93-09/14/94

Objective: To understand the spatial and temporal ozone and temperature distribution (and changes).

Product: An improved database to determine the trend in midlatitude ozone.

Approach: Extensive statistical analyses will be carried out on the data sets of ozone and temperature from the Total Ozone Mapping Spectrometer (TOMS), Stratospheric Backscatter Ultraviolet (SBUV), Stratospheric Aerosol and Gas Experiment (SAGE II), and NOAA Umkehr Network in an attempt to determine spatial and seasonal ozone and temperature trends (and their interrelationships) as a function of latitude, longitude, and altitude. CFCs, CO₂, CH₄, sulfates, and other species will be included in the analyses. Multiple regression techniques will be employed with ozone and/or temperature as dependent variables. Latitude, longitude, quasibiennial oscillation, and solar variability will be examined as the independent variables. Although the four data sets overlap temporally, the different measurement systems yield differing ozone data sets. Further, the models and measurements do not agree.

This research will assist in understanding and reducing the differences.

The physical relationship between derived lower stratospheric ozone trends at midlatitudes and observed atmospheric temperature trends will be investigated. Whether derived global mean temperature trends in the lower stratosphere can be produced by reduced radiative heating caused by observed ozone losses is questionable because the temperature trends are largest at low latitudes while the ozone trends are largest at midlatitudes. The tropical cooling of the lower stratosphere may be reducing the rate of transport of ozone to higher latitudes thereby producing the negative ozone trend at midlatitudes. The tropical stratospheric cooling may be a consequence of increasing concentrations of radiatively active gases, such as CO₂. Model calculations and trend analyses of stratospheric transport parameters will be conducted to investigate this possibility.

Results to Date: New project.

INVESTIGATION OF THE EFFECT OF NATURAL PHENOMENA AND INDUSTRIAL ACTIVITY ON STRATOSPHERIC OZONE TRENDS

McELROY, MICHAEL B.

HARVARD UNIVERSITY

FY 1993	168
FY 1992	0
FY 1991	0

09/15/93-09/14/94

Objective: To assess natural perturbations in the ozone and to improve analyses of changes in ozone caused by industrial emissions.

Product: An improved understanding of the physical process that perturbs stratospheric ozone.

Approach: The available data on the distribution and concentration of stratospheric ozone will be evaluated to assess natural causes of perturbation in the ozone (e.g., the solar cycle and volcanic injections of aerosols) and to improve analyses of changes in ozone caused by industrial emissions. The Dobson (ground-based total ozone measurements) and TOMS (satellite measurements of total ozone) data will be analyzed for

changes related to the quasibiennial oscillation of the equatorial winds (QBO), the El Niño/Southern Oscillation (ENSO), solar activity, and volcanic activity. Residuals of the monthly ozone means will be compared with indices of the QBO and ENSO. Solar-activity influences will be addressed with locally weighted regression techniques to focus on low-frequency variations. Because volcanic eruptions are not uniformly distributed in time and space, ground- and space-based atmospheric-extinction data will be used to assess the impact of aerosols on the measurements of ozone. Ozone-sonde data, which are the only measurements of the vertical distribution of ozone through the troposphere and stratosphere but which exhibit instrument artifacts, will be analyzed in a similar manner as the Dobson and TOMS data, with a focus on the temporal trend at each station.

A radiative-convective model will be used to compute mean, net heating rates and residual circulation. The model will include trace gases, aerosols, and tropospheric clouds. The calculations will be used to develop an index related to circulation changes that can be used in the analysis of the ozone trends. A global chemical model will be used to investigate the chemical effects on ozone of solar activity, volcanic aerosols in the stratosphere, and changes in abundances of trace gases, including CFCs, CH₄, and N₂O. The global mean distribution of ozone will be calculated as a function of altitude and time.

Results to Date: New project.

SAGE II-UMKEHR OZONE COMPARISONS AND AEROSOL EFFECTS: AN EMPIRICAL AND THEORETICAL STUDY

NEWCHURCH, MICHAEL J.

UNIVERSITY OF ALABAMA

FY 1993	190
FY 1992	0
FY 1991	0

09/15/93-09/14/94

Objective: To examine the impact of aerosols on the quality of the data from measurements of vertical ozone profiles.

Product: An improved understanding of the impact of aerosols on stratospheric-ozone-measurement techniques and on stratospheric-ozone trends.

Approach: The interference of stratospheric aerosols with the detection and measurement of vertical ozone profiles will be investigated by comparing SAGE II data with Umkehr data. This comparison will include statistical analysis and hypothesis testing of potential relationships between Umkehr and SAGE II measurements. The comparison will allow the data to be corrected for interference and the assessment of ozone concentration trends in the stratosphere.

A modeling study will be conducted that will include how the aerosols influence the radiative transfer and the wavelengths in the Umkehr inversion to determine ozone profiles. Background aerosols as well as the Mt. Pinatubo events will be considered. A number of additional parameters will be also be included in the analysis such as climatology, season, latitude, longitude, and particular station characteristics. The model study will account for multiple scattering and anisotropic scattering and will use two separate radiative transfer models: the JPL/Cal Tech (Jet Propulsion Laboratory/California Institute of Technology) model and the University of Arizona model.

Results to Date: New project.

SENSITIVITY AND UNCERTAINTY ANALYSIS OF ATMOSPHERIC-OZONE PHOTOCHEMISTRY MODELS

SMITH, GREGORY P.

SRI INTERNATIONAL

FY 1993	200
FY 1992	0
FY 1991	0

09/30/93-09/29/94

Objective: To determine the sensitivities and uncertainties associated with chemical-kinetics models of the global atmospheric ozone.

Product: An assessment of the uncertainty in the models and thus a basis for model improvement.

Approach: The current chemical-kinetics models of the global atmospheric ozone couple photolysis, chemical rate constants, transport, and dynamics. The effects of elementary rate constants and in the atmospheric kinetics on the performance of these models will be investigated by compiling and developing information on the kinetics parameterizations, the basic atmospheric conditions used in reduced-form models (0-D models), and the direct sensitivity calculation codes Chemkin/Senkin. A well-tested framework will be used for the analysis. The Chemkin code provides gas-phase and gas-surface chemical reactions and thermodynamics and a first-order sensitivity analysis. The uncertainties associated with the rate constants and the kinetics data

will be analyzed directly with the Chemkin/Senkin codes. To test for possible higher-order interaction, a series of repeat calculations will be conducted varying key rate constants individually and in pairs. The results will be compared with the first-order sensitivity calculations. Collective sensitivities and uncertainties will be calculated for ozone and other selected species with the rate constant and kinetic-sensitivity information. Optimization techniques and 1-D atmospheric modeling codes will be used to evaluate the net uncertainty in ozone modeling.

Results to Date: New project.

SUPPORT OPERATIONS

The objective is to provide an instrumented, twin-turboprop atmospheric-research aircraft for direct access by DOE research projects with the possibility of secondary access by non-DOE clients.

The aircraft chosen for this purpose, a Gulfstream-1 (G-1), has been selected on the basis of its performance characteristics (range, speed, altitude, carrying capacity, and economy) in reflection of DOE programmatic needs. The aircraft has been extensively instrumented for air-chemistry, cloud-chemistry, and cloud-physics measurements.

The following example applications illustrate DOE uses of this facility.

Kuwait Oil-Fire Evaluation: During FY 1991 (July-August 1991), DOE contributed to a multinational effort, coordinated under the World Meteorological Organization, to characterize the atmospheric, climatological, and biological effects of the Kuwait oil fires. As a part of this effort, DOE dispatched the G-1 to the Arabian Gulf region for extensive plume measurements at close and extended distances downwind from the source region. The G-1's instrument ensemble included equipment for measuring aerosol physical and chemical properties, concentrations of organic and inorganic pollutant gases, cloud-nucleating properties, and solar/terrestrial radiation. Approximately 15 research flights were conducted during this series, and the resulting data are being pooled with the international effort for joint interpretation.

The G-1 research aircraft was developed with the expectation that DOE would play a major role in future global-scale atmospheric research as a part of its implementation and development of the EPACT. This process is now beginning to occur,

and as a result, extensive DOE application of the G-1 is anticipated under its Atmospheric Chemistry Program (ACP; programmatic emphasis: continental and oceanic fate of energy-related air pollutants) and its Atmospheric Radiation Measurement (ARM) Program.

The current G-1 mission is an ACP flight series over the North Atlantic in coordination with the international North Atlantic Regional Experiment (NARE) Program.

Research instrumentation for the G-1 is continually being developed and upgraded as these applications occur. The most recent and ambitious instrument-development effort to date has been the modification of a tandem mass spectrometer for G-1 use. This instrument will provide the aircraft with part-per-trillion measurement capability for a large number of important pollutant species and the possibility of emission/deposition flux determination.

Program Managers

Michael R. Riches
Environmental Sciences Division
ER-74
Department of Energy
Washington, DC 20585
301-353-3264

Principal Scientist

Jeremy M. Hales
Envair
4811 W. 18th Ave.
Kennewick, WA 99337
509-735-9480

Research Summary

RESEARCH AIRCRAFT OPERATIONS

BUSNESS, KENNETH M.

PACIFIC NORTHWEST LABORATORY

FY 1993	370
FY 1992	750
FY 1991	750

10/01/92-09/30/93

Objective: To conduct airborne sampling with enhanced high-altitude and in-storm operation capability.

Product: Airborne measurement capabilities necessary to supply the diagnostic environmental measurements demanded by modern interpretive modeling techniques.

Approach: A twin-turboprop research aircraft will be provided under the direction of the Atmospheric Sciences Department, PNL. Operations will be designed to provide direct access to the aircraft for DOE projects that have the possibility for secondary access by non-DOE clients.

Results to Date: Late in FY 1992, the G-1 aircraft was employed in a "pre-NARE" (North Atlantic Regional Experiment) ACP field study. Based in Halifax, Nova Scotia, the G-1 flew 21 missions in the western North Atlantic region, characterizing pollutant transport and

aerosol properties and evaluating the performance of new instrumentation. Following the month-long field study, the G-1 was deployed to Boulder, Colorado, where personnel from PNL and ANL conducted tests of the aircraft's gust probe system by means of instrumented tower fly-bys.

Following upgrades of meteorological and electrical power systems, the G-1 will again be deployed to the western North Atlantic to participate in the 1993 NARE multiagency effort. At least three aircraft will be involved in this study, conducting sampling missions from the northeast coastal U.S. to eastern Nova Scotia and surrounding maritime regions. The G-1 will again be carrying personnel and instruments from BNL and PNL for studying vertical and horizontal transport of North American pollutants, photochemical processes, and aerosol composition.

In 1993, plans were initiated to restructure the PNL aircraft operation to function as a DOE research aircraft facility. In this arrangement, the aircraft and support personnel at PNL will be base-funded for an annual block of flight hours (on the order of 250 to 300 hours) to provide flight operations for all DOE researchers. Flight hours will be allocated to successful DOE proposers for use in their research activities at essentially no cost to their programs. PNL will maintain the aircraft and an extensive suite of instruments for use by the entire DOE community. This arrangement is expected to be implemented in FY 1995.

APPENDIX A: ADDRESSES OF PRINCIPAL INVESTIGATORS

Addis, Robert P.
Westinghouse Savannah River Co.
P.O. Box 616
Aiken, SC 29802
803-725-3325

Aker, Pamela M.
Department of Chemistry
234 Chevron Science Center
University of Pittsburgh
Pittsburgh, PA 15260
412-624-8500

Allwine, K. Jerry
Pacific Northwest Laboratory
P.O. Box 999
Richland, WA 99352
509-376-8145

Berkowitz, Carl M.
Pacific Northwest Laboratory
P.O. Box 999
Richland, WA 99352
509-376-6460

Bossert, James
Los Alamos National Laboratory
P.O. Box 1663
Los Alamos, NM 87545
505-667-6268

Busness, Kenneth M.
Pacific Northwest Laboratory
P.O. Box 999
Richland, WA 99352
509-376-4503

Coulter, R. L.
Argonne National Laboratory
9600 S. Cass Ave.
Argonne, IL 60439
708-252-5833

Daum, Peter
Applied Sciences Division
Brookhaven National Laboratory
Upton, NY 11973
516-282-7283

Davidovits, Paul
Department of Chemistry
Boston College
Chestnut Hill, MA 02167
617-552-3617

Dietz, Russell N.
Applied Sciences Division
Brookhaven National Laboratory
Upton, NY 11973
516-282-3059

Doran, J. Christopher
Pacific Northwest Laboratory
P.O. Box 999
Richland, WA 99352
509-376-4734

Finlayson-Pitts, B. J.
Departments of Chemistry and Biochemistry
California State University at Fullerton
Fullerton, CA 92634-9408
714-773-2661

Gaffney, J. S.
Argonne National Laboratory
9600 S. Cass Ave.
Argonne, IL 60439
708-252-5178

Greenfield, Richard S.
National Science Foundation
1800 G St NW
Washington, DC 20550
202-357-7645

Gudiksen, Paul H.
Lawrence Livermore National Laboratory
P.O. Box 808
Livermore, CA 94550
510-422-1813

Heit, Merrill
DOE/Environmental Measurements Laboratory
376 Hudson St.
New York, NY 10014-3621
212-620-3623

Hofmann, David J.
NOAA/CMDL, R/E/CG1
325 Broadway
Boulder, CO 80303-3328
303-497-6663

Hood, Lon L.
Lunar and Planetary Laboratory
University of Arizona
Tucson, AZ 85721
602-576-1248

Hosker, R. P., Jr.
Atmospheric Turbulence and Diffusion Division
NOAA
456 South Illinois Ave.
P.O. Box 2456
Oak Ridge, TN 37831-2456
615-576-1248

Kleinman, Lawrence I.
Applied Sciences Division
Brookhaven National Laboratory
Upton, NY 11973
516-282-3796

Lee, J. T.
Los Alamos National Laboratory
P.O. Box 1663
Los Alamos, NM 87545
505-667-8352

Lee, Yin-Nan
Applied Sciences Division
Brookhaven National Laboratory
Upton, NY 11973
516-282-3294

Leone, John M., Jr.
Lawrence Livermore National Laboratory
P.O. Box 808
Livermore, CA 94550
510-422-6449

Lindberg, Steven E.
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831
615-574-7857

Marley, N. A.
Argonne National Laboratory
9700 S. Cass Ave.
Argonne, IL 60439
708-252-5014

Marlow, William H.
Texas Engineering Experiment Station
380 Wisenbaker Engineering Research Center
College Station, TX 77843
409-845-2271

McElroy, Michael B.
Division of Applied Sciences
Pierce Hall
Harvard University
Cambridge, MA 02138
617-495-4359

McMurry, Peter H.
Department of Mechanical Engineering
University of Minnesota
111 Church St., SE
Minneapolis, MN 55455
612-625-3345

Moyers, Jarvis L.
National Science Foundation
1800 G St NW
Washington, DC 20550
202-357-9657

Newchurch, Michael J.
University of Alabama Research Institute
Huntsville, AL 35899
205-895-6458

Newman, Leonard
Bldg. 426
Environmental Chemistry Division
Brookhaven National Laboratory
Upton, NY 11973
516-282-4467

Novakov, Tihomir
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, CA 94720
415-486-5319

Penner, Joyce E.
Lawrence Livermore National Laboratory
P.O. Box 808
Livermore, CA 94550
510-422-4140

Shannon, J. D.
Argonne National Laboratory
9700 S. Cass Ave.
Argonne, IL 60439
708-252-5807

Shaw, William J.
Pacific Northwest Laboratory
P.O. Box 999
Richland, WA 99352
509-376-4603

Smith, Gregory P.
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025
415-859-3496

Tang, Ignatius N.
Applied Sciences Division
Brookhaven National Laboratory
Upton, NY 11973
516-282-4517

Weinstein-Lloyd, Judith B.
Chemistry/Physics Department
University of New York at Old Westbury
P.O. Box 210
Old Westbury, NY 11568
516-876-2743

Wesely, Marvin L.
Argonne National Laboratory
9700 S. Cass Ave.
Argonne, IL 60439
708-252-5827

Whiteman, C. David
Pacific Northwest Laboratory
P.O. Box 999
Richland, WA 99352
509-376-7859

APPENDIX B:

ACRONYMS

4DDA	Four-dimensional data assimilation
ACCESS	Atmospheric Chemistry Colloquium for Emerging Senior Scientists
ACP	Atmospheric Chemistry Program
AES	Atmospheric Environment Service (of Canada)
AMS	American Meteorological Society
ANL	Argonne National Laboratory
ARAC	Atmospheric Release Advisory Capability [Program]
ARM	Atmospheric Radiation Measurement [Program]
ASCOT	Atmospheric Studies in Complex Terrain
ATDD	Atmospheric Turbulence and Diffusion Division (NOAA)
BASC	Board on Atmospheric Science and Climate
BNL	Brookhaven National Laboratory
CARS	coherent anti-Stokes Raman scattering
CCM	community climate model
CCN	cloud condensation nuclei
CEC	Commission of European Communities
CEES	Committee on Earth and Environmental Sciences
CLOT	Carbon layer open tubular (capillary column)
COPS	continuously operating perfluorocarbon analyzer
CSU	Colorado State University
DMS	dimethyl sulfide
DMSO	Dimethyl sulfoxide
DMSO ₂	Dimethyl sulfone
DTA	Dual-trap analyzer
EG&G	Edgerton, Germeshauser, and Greer
ENSO	El Niño/Southern Oscillation
EPACT	Energy Policy Act (of 1992)
EPER	Environmental Processes and Effects Research [Program]
ER	Energy Research
ESD	Environmental Sciences Division
FBS	Frontal Boundary Study
FCCSET	Federal Coordination Council for Science, Engineering, and Technology
FID	flame ionization detector
FTIR	Fourier transform infrared
FTS	full turbulence simulation
G-1	Gulfstream-1 [airplane]
GC	gas chromatography
GChM	Global Chemistry Model
HC2	Glycoaldehyde
HMS	Hanford Meteorological Station
IGAC	International Global Atmospheric Chemistry [Program]

INS	inertial navigation system
IPCC	Intergovernmental Panel on Climate Change
JPL	Jet Propulsion Laboratory
LANL	Los Alamos National Laboratory
LBL	Lawrence Berkeley Laboratory
LLNL	Lawrence Livermore National Laboratory
LPDM	Lagrangian particle dispersion model
MDSRS	morphology-dependent simulated Raman scattering
MLOPEX II	Mauna Loa Observatory Photochemical Experiment II
MOU	Memorandum of understanding
MS	mass spectrometry
MSA	Methane sulfonic acid
NARE	North Atlantic Regional Experiment
NCAR	National Center for Atmospheric Research
NES	National Energy Strategy
NMHC	Nonmethane hydrocarbon
NOAA	National Oceanic and Atmospheric Administration
NSF	National Science Foundation
ocPDCH	Ortho(cis)-perfluorodimethylcyclohexane
OHER	Office of Health and Environmental Research
PAH	Polyaromatic hydrocarbon
PAN	peroxyacetyl nitrate
PBL	planetary boundary layer
PCDD	Polychlorinated dibenzodioxin
PCDF	Polychlorinated dibenzofuran
PFCs	perfluorocarbon compounds
PFTs	perfluorocarbon tracers
PM-10	particulate matter less than 10 micrometers
PNL	Pacific Northwest Laboratory
PSU	Pennsylvania State University
QBO	Quasibiennial oscillation
RAMS	regional atmospheric modeling system
RASS	radio acoustic sounding system
SAGE	Stratospheric Aerosol and Gas Experiment
SAR	Subcommittee on Atmospheric Research
SBUV	Stratospheric Backscatter Ultraviolet (satellite)
SERON	Southeastern Regional Oxidant Network
SOS	Southern Oxidant Study
SRS	Savannah River Site
TAGA	trace atmospheric gas analyzer
TDMA	tandem differential mobility analyzer
TF	throughfall
TOMS	Total Ozone Mapping Spectrometer (satellite)
UFACNC	ultrafine aerosol condensation nucleus counter
UNEP	United Nations Environment Programme
USGCRP	United States Global Change Research Program
UV	ultraviolet
UV-B	ultraviolet type B
UV-vis	ultraviolet-visible
WGGC	Working Group on Global Change
WMO	World Meteorological Organization

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