



RESEARCH REPORT
1987-89

ENVIRONMENTAL QUALITY LABORATORY
AND
ENVIRONMENTAL ENGINEERING SCIENCE
W. M. KECK LABORATORIES

Division of Engineering and Applied Science
CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

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CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91125

EQL Report No. 31

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TABLE OF CONTENTS

	<u>Page</u>
PREFACE	v
ENVIRONMENTAL QUALITY LABORATORY	1
ENVIRONMENTAL ENGINEERING SCIENCE	3
PROFESSORIAL FACULTY	5
RESEARCH STAFF 1987-1989	7
VISITORS AND CONSULTANTS	9
CURRENT SUPPORT STAFF	11
GRADUATE STUDENTS	12
DOCTORAL THESES COMPLETED, 1987-89	14
SPONSORS AND DONORS	18
SUMMARIES OF RESEARCH PROJECTS, 1987-89	21
LIST OF PROJECTS	27
A. WATER QUALITY AND AQUATIC CHEMISTRY	27
B. APPLIED AND ENVIRONMENTAL BIOLOGY	43
C. ENVIRONMENTAL HYDRAULICS AND COASTAL ENGINEERING	51
D. AIR QUALITY, ATMOSPHERIC CHEMISTRY AND AEROSOL PHYSICS	79
E. RISK ASSESSMENT AND REGULATION	
BOOKS PUBLISHED, 1987-89	113
CONFERENCES, 1987-89	113

PREFACE

This research biennial report for 1987-89 covers the activities of both the Environmental Engineering Science program and the Environmental Quality Laboratory for the period October 1987-November 1989. Environmental Engineering Science is the degree-granting academic program housed in the Keck Laboratories, with associated research projects. The Environmental Quality Laboratory is a research center focusing on large scale problems of environmental quality and natural resources. All the faculty and students involved in EQL projects are part of one of the regular academic programs, with the largest number being in Environmental Engineering Science. Hence the convenience of this combined report.

In the lists of students, degrees, and research projects we have included some students in other degree programs who are working on environmental topics under one of the professors associated with EES and/or EQL. Caltech's small size and flexible structure allows professors to participate in more than one academic program including the supervision of doctoral students.

The report starts with brief descriptions of EQL and EES, then lists the people - professors, research staff, visitors and consultants, support staff, and graduate students. Next is a listing of our research sponsors and donors, to whom we are all indebted for making these programs possible. The main part of the report presents the research summaries for all our activities including publications during the period October 1987 - November 1989. Also included at the end of the report is a listing of books published during 1987-89 (which do not appear in the research summaries) and information about a major smog conference held in 1988.

For more information or for copies of any publications write to the appropriate professor, or Publications Secretary for EQL and EES, Keck Laboratories 138-78, Caltech, Pasadena, California 91125. Requests to professors or the publications secretary may also be sent by FAX to (818) 356-2940.

It is hoped this report will be a useful reference not only for prospective students and visitors but also for the entire EES and EQL group.

Norman H. Brooks
Director of EQL, and
Executive Officer for EES

ENVIRONMENTAL QUALITY LABORATORY

The Environmental Quality Laboratory at Caltech is a center for research on large-scale systems problems of natural resources and environmental quality. The principal areas of investigation at EQL are:

1. Air quality management.
2. Water resources and water quality management.
3. Control of hazardous substances in the environment.
4. Energy policy, including regulation, conservation and energy-environment tradeoffs.
5. Resources policy (other than energy); residuals management.

EQL research includes technical assessments, computer modeling, studies of environmental control options, policy analyses, and research on important components of the large-scale systems. Field work is also undertaken by EQL, some in collaboration with other organizations, to provide critical data needed for evaluation of systems concepts and models. Needed laboratory research is done through EES laboratories in the Keck Engineering Laboratories building.

EQL's objectives are as follows:

1. *To do systematic studies of environmental and resources problems.* The results of these studies, including the clarification of policy alternatives, are communicated to decision-makers in government and industry, to the research community, and to the public. As an organization, EQL refrains from advocating particular policies, but seeks to point out the implications of the various policy alternatives.
2. *To contribute to the education and training of people in these areas* through involvement of predoctoral students, postdoctoral fellows, and visiting faculty members in EQL activities. This educational effort is just as important as the results of the studies themselves, and should make lasting contributions to the nation's ability to solve its environmental and resources problems.

The work at EQL goes beyond the usual academic research in that it tries to organize and develop the knowledge necessary to clarify society's alternatives by integrating relevant disciplines. EQL works on solving problems of specific localities when there is a strong element of public interest or educational value, or the concepts and results are applicable to other places.

The research of EQL during this period was done under the supervision of faculty members in Environmental Engineering Science, Chemical Engineering, and Social Science.

ENVIRONMENTAL ENGINEERING SCIENCE

This interdisciplinary graduate program is concerned with the protection and control of the environment. Research and instruction stress basic studies that aim to answer such questions as: How can we improve the air quality in urban and industrial centers while maintaining clean air in pristine rural areas? How can we ensure a supply of water of adequate quality and quantity for population centers and industry? How can we safeguard the marine environment from pollution? What are the environmental consequences of alternative modes of energy production?

The academic disciplines of importance to the program include chemistry and physics of natural waters and atmospheres; physics and chemistry of particles; applied microbiology, marine biology and ecology; fluid mechanics of the natural environment; hydrology; pollutant formation and control in combustion systems; theory and design of complex environmental control systems; environmental modeling and monitoring systems; and processes of erosion, coagulation and sedimentation. Courses offered in the Environmental Engineering Science program and in other related programs of the Institute are listed in the Caltech catalog. Faculty members participating in this interdisciplinary program are from the Divisions of Engineering and Applied Science, and Chemistry and Chemical Engineering.

Areas of Research

Examples of recent and current research are theoretical and experimental studies on fates of trace elements in the environment; coagulation and settling of particles in seawater; aerosol chemistry and physics; acid rain and fog; interactions between toxicants and marine kelp; kinetics of oxidation processes in aqueous systems; genetics and physiology of microbial transformations; in situ bioremediation processes; pollutant and particle transport in alluvial streams and groundwaters; dilution in turbulent shear flows; role of buoyancy forces in turbulent mixing; buoyant discharges in coastal waters; pollutant formation and control in combustion; regional air pollution modeling and control; and effects of air pollutants on works of art.

Physical Facilities

The laboratory experimental work in environmental engineering science is primarily carried out in the W. M. Keck Laboratories with a wide variety of modern instrumentation in the various laboratories described in detail in the Caltech catalog. The principal components are air quality laboratories (including a roof-top smog chamber), water quality laboratories, hydraulics laboratory, applied microbiology laboratory, and part of the Kerckhoff Marine Laboratory (at Corona del Mar) used for marine ecology. Except for the latter all laboratories are housed in the Keck Engineering Laboratories building.

An excellent library with a wide variety of current materials in environmental engineering and science, and hydraulics, is centrally located in the Keck Laboratories building.

The department provides students with access to scientific computing and word processing through various departmental computers and peripheral devices and the CADRE network of VAXs operated by the Division of Engineering and Applied Science and the EQL VAX.

Academic Program

The academic program is oriented toward the Ph.D. degree, although the M.S. degree is also offered for those more interested in engineering practice or administration than teaching, research, or advanced engineering work. The enrollment for the Fall Term (1989-90) included twenty-one Ph.D. students and two M.S. students. The primary faculty group includes ten professors (Brooks, Cass, Flagan, Hoffmann, Lidstrom, List, Morgan, North, Raichlen, Seinfeld); their full titles and description of interests are given on pp. 5-6.

These core professors also supervise some students from other academic programs in their research groups, and hence their research and theses are included also. Of particular note are Civil Engineering students specializing in environmental hydraulics and coastal engineering, and Mechanical Engineering and Chemical Engineering students in air pollution.

PROFESSORIAL FACULTY

NORMAN H. BROOKS, *James Irvine Professor of Environmental and Civil Engineering; Executive Officer for Environmental Engineering Science; Director, Environmental Quality Laboratory*

Hydrology; dispersion; wastewater disposal; sediment and pollutant transport; hydraulic and environmental engineering.

GLEN R. CASS, *Professor, Environmental Engineering and Mechanical Engineering*

Air quality management; control strategies for sulfur oxides, nitrogen oxides, oxidants, and particulate air pollutants; visibility; protection of works of art from environmental damage; indoor air quality.

JEFFREY A. DUBIN, *Associate Professor, Economics*

Econometric theory and methodology; applied statistical modeling; energy economics; public finance; law and economics.

RICHARD C. FLAGAN, *Professor, Environmental Engineering Science and Mechanical Engineering*

Coal combustion; nucleation; mechanisms of pollutant formation and control; aerosol physics and chemistry; aerosol instrumentation; atmospheric aerosols; aerosol processing of materials.

MICHAEL R. HOFFMANN, *Professor, Environmental Engineering Science*

Applied chemical kinetics; redox reactions, auto-oxidations, and hydrolysis reactions; characterizations of the detailed reaction kinetics and mechanisms of the metal catalyzed reactions of organic esters, substituted phenolic compounds, and reduced sulfur compounds; homogeneous, heterogeneous, microbial , and photo-assisted catalysis; cloud and fog chemistry and physics; semiconductor synthesis; synthesis of superconducting precursors.

MARY E. LIDSTROM, *Associate Professor, Applied Microbiology*

Methylotrophic bacteria; gene organization and expression; physiology of growth on one-carbon compounds; biochemistry of C-1 enzymes; role of methylotrophs in global carbon cycling in natural environments; use of methylotrophs in detoxification of halogenated hydrocarbons; commercial exploitation of methylotrophs for biocatalysis.

E. JOHN LIST, *Professor, Environmental Engineering Science*

Turbulent mixing processes, buoyancy-driven flows, gas transfer at liquid interfaces, particle coagulation.

PROFESSORIAL FACULTY (cont.)

RICHARD D. McKELVEY, *Professor, Political Science*

Game theory; theory of political decisions; group decision making; voting behavior and elections.

JAMES J. MORGAN, *Marvin L. Goldberger Professor of Environmental Engineering Science*

Aquatic chemistry, surface chemistry in water, coagulation processes; kinetics of oxidation processes in water.

WHEELER J. NORTH, *Professor, Environmental Science*

Marine-oriented ecological research impacts of waste disposal into the coastal environment, improved management of living marine resources, and possibilities of marine biomass as an alternative energy source.

CHARLES R. PLOTT, *Edward S. Harkness Professor of Economics and Social Science*

The influence of rules and procedures on the behavior of markets, committees, and elections; development of mathematical techniques and experimental methods as tools for analysis in these areas; applications in areas of market research, organizational decisions, antitrust policy, and regulatory policy and politics.

FREDRIC RAICHLEN, *Professor, Civil Engineering*

Coastal engineering; wave mechanics and wave-structure interactions in near-shore regions; dynamics of harbors exposed to continuous and transient waves; mechanics of tsunamis including generation, propagation, and coastal effects; the mechanics of breaking waves and their effects at the coastline.

JOHN H. SEINFELD, *Louis E. Nohl Professor and Professor, Chemical Engineering; Chairman, Division of Engineering and Applied Science, effective April 1, 1990*

Atmospheric chemical engineering; the physics and chemistry of the atmospheric behavior of air pollutants, both gaseous and particulate; mathematical modeling of the polluted atmosphere; aerosol dynamics and growth.

VITO A. VANONI, *Professor of Hydraulics, Emeritus*

Sediment transport, river engineering, hydraulic structures, and hydrology.

THEODORE Y.-T. WU, *Professor of Engineering Science*

Wave hydrodynamics, propulsion, geo- and biophysical fluid mechanics.

RESEARCH STAFF 1987 - 1989

<u>Name</u>	<u>Title</u>	<u>Dates</u>
Peggy J. Arps (Microbiology)	Senior Research Fellow	9/87-8/89
Bruce Daube, Jr. (Instrumentation for lab and field)	Research Engineer	6/85-12/89
Alan DiSpirito (Microbiology)	Sr. Research Fellow	8/87-8/89
Panos Georgopoulos (Air quality modeling)	Senior Research Engineer	3/86-8/89
Dieter Gunz (Aquatic chemistry)	Research Fellow	10/87-9/89
Robert C. Y. Koh (Hydraulics, water quality modeling)	Senior Research Associate Member of Professional Staff (part-time)	8/72-11/88 11/88-
Jochen Kraft (Aquatic chemistry)	Research Fellow	1/88-1/89
Michael Kuhn (Microbiology)	Research Fellow	10/87-12/88
Mary P. Ligocki (Air quality sampling and measurement)	Research Scientist	3/87-7/89
Monica A. Mazurek (Air pollution chemistry)	Research Fellow Scientist	2/86-2/89 2/89-6/89
Kenneth F. McCue (Computer specialist)	Scientist	8/83-
German Mills (Aquatic chemistry)	Research Fellow	7/87 - 2/89

RESEARCH STAFF (cont.)

Christina Morris (Microbiology)	Research Associate	9/89-
Lynn Salmon (Air quality laboratory)	Research Engineer	9/86-
Paul A. Solomon (Air pollution chemistry)	Scientist	12/84-3/88
Brenda Speer (Microbiology)	Research Fellow	9/89-8/90
Daryle Waechter-Bruna (Microbiology)	Research Associate	8/88-8/90
George T. Yates (Hydrodynamics)	Member of Professional Staff	85-
Jeffrey Zelt (Coastal engineering)	Research Fellow	5/89-11/89

VISITORS AND CONSULTANTS

Eric Betterton (Aquatic chemistry)	Visiting Scientist in Environmental Engineering Science	6/87-6/88
Colleen Cavanaugh (Microbiology)	Visiting Associate in Environmental Engineering Science (from Harvard University)	1/88-7/88
Daniel Grosjean (Air quality)	Visiting Associate in Chemical Engineering	
Steven J. Eisenreich (Aquatic chemistry)	Visiting Associate in Environmental Engineering Science (from University of Minnesota)	1/88-3/88
Philip M. Gschwend (Aquatic chemistry)	Visiting Associate in Environmental Engineering Science (from Massachusetts Institute of Technology)	1/88-7/88
Susanne V. Hering (Air pollution)	Visiting Associate in Chemical Engineering	8/89-
Susan M. Larson (Visibility)	Consultant, EQL (from University of Illinois)	Summer 1989
Gregory Markowski (Air pollution sampling)	Consultant, EQL	4/84-6/89
Monica A. Mazurek (Air pollution chemistry)	Visiting Associate in Environmental Engineering Science (from Brookhaven National Laboratories)	7/89-
Nobuo Mimura (Hydraulics)	Visiting Associate in Civil Engineering	9/87 - 9/88

VISITORS AND CONSULTANTS (cont.)

Alexander Netrusov (Microbiology)	Visiting Scientist in Environmental Engineering Science (from University of Moscow)	3/87-5/87
Christodoulos Pilinis (Air quality modeling)	Visiting Associate in Environmental Engineering Science (from Aerovironment)	5/88-
David Porter (Resource economics)	Visiting Associate in Economics (from JPL)	11/87-4/88
Armistead Russell (Air quality modeling)	Co-investigator with Prof. Glen Cass (from Carnegie Mellon University)	7/89-
Keith Stolzenbach (Environmental fluid mechanics)	Visiting Associate in Environmental Engineering Science (from Massachusetts Institute of Technology)	6/89-9/89
Bernard Wehrli (Water quality, geochemical cycles)	Visiting Associate in Environmental Engineering Science (from EAWAG, Dubendorf, Switzerland)	9/87-9/88

CURRENT SUPPORT STAFF

ENVIRONMENTAL ENGINEERING SCIENCE

Sandra R. Brooks	Senior Administrative Secretary
William J. Brulla	Associate Biologist
Evelina E. Cui	Senior Administrative Secretary
Richard Eastvedt	Senior Mechanic
Joseph Fontana	Machine Specialist
Elaine Granger	Senior Administrative Secretary
Rayma Harrison	Librarian
Gunilla Hastrup	Senior Library Assistant
Eun K. Lee	Research Assistant
Frances Matzen	Senior Administrative Secretary
Hai Duc Vu	Assistant Engineer

ENVIRONMENTAL QUALITY LABORATORY

Christine Colegate	Senior Administrative Secretary
Patricia Rankin	Assistant to the Director, EQL
Nancy Tomer	Senior Drafter

GRADUATE STUDENTS

1987-88

<u>Name</u>	Degree Option#	<u>Name</u>	Degree Option#
Adamson, Joel W.*	EES	Nazaroff, William W.*	EES
Collett, Jeffrey Lee	EES	Ng, Kit Yin	EES
Cutts, Stephen	EES	Nguyen, Hung	ChE
DiChristina, Thomas	EES	Olson, Terese	EES
Elliott, Alexander	EES	Palma, Luiz	EES
Erel, Yigal*	Geo	Pandis, Spyros N.*	ChE
Fuhs, Susan E.	ME	Petroff, Catherine	CE
Grader, Gideon S.	ChE	Pilinis, Christodoulos*	EES
Grant, Lisa	EES	Ramsden, Jerald	CE
Grant, Stanley B.*	EES	Rasi, Marco	CE
Harley, Robert A.*	EES	Rogak, Steve	EES
Hildemann, Lynn M.*	EES	Rogge, Wolfgang F.*	EES
Horrell, Robin S.*	ChE	Sahu, Ranajit	ME
James, David E.*	EES	Schlautman, Mark A.*	EES
Jun, Kyung Soo	CE	Scott, Michael J.*	EES
Kim, Yong P.*	ChE	Shi, Guojun*	EES
Kormann, Claudius	Ch	Ting, Francis	CE
Kotronarou, Anastassia	EES	Torry, Lori	EES
Krema-DiSpirito, Cinder	EES	Valdes, Alberto	CE
Levendis, Yiannis	EES	Wang, Shih-chen	EES
Li, Xiaoming	EES	Wang, Rueen-Fang T.*	EES
Liang, Liyuan*	EES	Wexler, Anthony S.*	ME
Mau, Russell E.*	CE	Wong, Brian	EES
Munger, James William	EES	Yee, Howell	EES
		Zeng, Langche*	SS

#CE =	Civil Engineering
Ch =	Chemistry
ChE =	Chemical Engineering
EES =	Environmental Engineering Science
Geo =	Geology
ME =	Mechanical Engineering
SS =	Social Science

*Supported by EQL, in full or in part.

GRADUATE STUDENTS

1988-89

<u>Name</u>	Degree <u>Option#</u>	<u>Name</u>	Degree <u>Option#</u>
Balaa, Talal	CE	Ng, Kit Yin	EES
Boylan, Richard T.*	SS	Nguyen, Hung	ChE
Christoforou, Christos*	ME	Olson, Mark A.*	SS
Collett, Jeffrey Lee*	EES	Pandis, Spyros N.*	ChE
DiChristina, Thomas*	EES	Paulson, Suzanne	EES
Dugan, Regina	ME	Petroff, Catherine	CE
Eldering, Annmarie*	EES	Ramsden, Jerald	CE
Elliott, Alexander H.*	EES	Rasi, Marco	CE
Fuhs, Susan E.	ME	Rogak, Steve	EES
Grant, Lisa	EES	Rogge, Wolfgang F.*	EES
Grant, Stanley B.*	EES	Ruilson, Aaron	ME
Harley, Robert A.*	EES	Schlautman, Mark A.*	EES
Hildemann, Lynn M.*	EES	Scott, Michael J.*	EES
Hoffman, Amy	Ch	Semrau, Jeremy*	EES
Horrell, Robin S.	ChE	Shi, Binqiang*	EES
James, David	EES	Shi, Guojun*	EES
Jun, Kyung Soo	CE	Stern, Jennifer	ChE
Kim, Yong P.*	ChE	Sullivan, Gregory A.	Aero
Kormann, Claudius	Ch	Ting, Francis	CE
Kotronarou, Anastassia*	EES	Wang, Shih-chen	EES
Krema-DiSpirito, Cinder	EES	Wexler, Anthony S.*	ME
Li, Xiaoming	EES	Wong, Brian	EES
Lunden, Melissa	ME	Yee, Howell	EES
Mau, Russell E.*	CE	Zhu, Qing	EES
Nelson, Christine	EES		

#CE =	Civil Engineering
Ch =	Chemistry
ChE =	Chemical Engineering
EES =	Environmental Engineering Science
Geo =	Geology
ME =	Mechanical Engineering
SS =	Social Science

*Supported by EQL, in full or in part.

DOCTORAL THESES COMPLETED

1987-88

CAROL LESLIE JONES ADKINS
Field: ChE
Advisor: J. H. Seinfeld

Use of a Continuous Stirred
Tank Reactor for the Study of
Aqueous Aerosol Chemistry

SUSAN ELIZABETH FUHS
Field: ME
Advisor: G. R. Cass

Studies of Inertial Deposition of
Particles onto Heat Exchanger Elements

PUI-KWAN ANDREW HONG
Field: EES
Advisor: M. R. Hoffmann

Catalytic Oxidation of Sulfur Dioxide by
Heterogeneous Cobalt-Phthalocyanine

SUSAN M. LARSON
Field: EES
Advisor: G. R. Cass

A Study of Summer Midday Low-Visibility
Events in the Los Angeles Area

YIANNIS ANGELO LEVENDIS
Field: EES
Advisor: R. C. Flagan

A Fundamental Study of Char Oxidation
Kinetics Using Model Materials

LIYUAN LIANG
Field: EES
Advisor: J. J. Morgan

Effects of Surface Chemistry on Kinetics of
Coagulation of Submicron Iron Particles
(α -Fe₂O₃) in Water

TERESE MARIE OLSON
Field: EES
Advisor: M. R. Hoffmann

The Formation Kinetics, Mechanisms, and
Thermodynamics of S(IV)-Aldehyde
Addition Compounds

DOCTORAL THESES COMPLETED (cont.)

1987-88 (cont.)

CHRISTODOULOS PILINIS
Field: EES
Advisor: J. H. Seinfeld

Mathematical Modeling of the Dynamics
and Thermodynamics of Multicomponent
Atmospheric Aerosols

RANAJIT SAHU
Field: ME
Advisor: R. C. Flagan

On the Combustion of Bituminous
Coal Chars

JENNIFER E. STERN
Field: ChE
Advisor: J. H. Seinfeld

Aerosol Formation and Growth in Aromatic
Hydrocarbon/NO_x Systems

RUEEN-FANG THERESA WANG
Field: EES
Advisor: N. H. Brooks

Laboratory Analysis of Settling Velocities of
Wastewater Particles in Seawater Using
Holography

DOCTORAL THESES COMPLETED

1988-89

JEFFREY LEE COLLETT

Field: EES

Advisor: M. R. Hoffmann

Characterization of Cloudwater and Precipitation Chemistry and Deposition at Elevated Sites in Central and Southern California

THOMAS J. DI CHRISTINA

Field: EES

Advisor: M. E. Lidstrom

Dissimilative Fe(III) Reduction by Alteromonas putrefaciens strain 200

DAVID E. JAMES

Field: EES

Advisor: W. J. North

Effects of Hydrazine and Other Toxicants on Early Life Stages of California Brown Algae

CLAUDIUS KORMANN

Field: Ch

Advisor: M. R. Hoffmann

Synthesis and Characterization of Quantum Size Metal Oxide Colloidal Particles. Photocatalytic Peroxide Formation on ZnO and TiO

JAMES WILLIAM MUNGER

Field: EES

Advisor: M. R. Hoffmann

The Chemical Composition of Fogs and Clouds in Southern California

WILLIAM W. NAZAROFF

Field: EES

Advisor: G. R. Cass

Mathematical Modeling and Control of Pollutant Dynamics in Indoor Air

MARCO RASI

Field: CE

Advisor: E. J. List

Mixing in Density-Stratified Flows

DOCTORAL THESES COMPLETED (cont.)

1988-89 (cont.)

FRANCIS CHI KIN TING
Field: CE
Advisor: F. Raichlen

Interaction of Water Waves with a Density-Stratified Fluid in Rectangular Trench

DOCTORAL THESES COMPLETED

1989-90*

LYNN M. HILDEMANN
Field: EES
Advisor: G. R. Cass

Origin of Atmospheric Organic Aerosols

KIT YIN NG
Field: EES
Advisor: N. H. Brooks

Thermal Plumes from Staged Multiport Diffusers in Uniform Quiescent Environment

*Completion of thesis by December, 1989.

SPONSORS AND DONORS

The staff and students of EQL and EES gratefully acknowledge the support of the following research sponsors and donors for fiscal years 1988 and 1989:

Environmental Quality Laboratory

Government Sponsored Projects

Regional

County Sanitation Districts
of Los Angeles County
South Coast Air Quality
Management District

State

California Air Resources
Board
Water Resources Center,
Univ. of California

Federal

Environmental Protection
Agency
National Aeronautics and
Space Administration
(through the Jet
Propulsion Laboratory)
National Science Foundation

Private Sources

Discretionary Funds-General

General Electric Foundation
General Motors
The William and Flora Hewlett
Foundation
Texaco Phil. Foundation

Discretionary Funds - Specific Program Areas

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Exxon Education Foundation
Andrew W. Mellon Foundation
Unocal

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Coordinating Research Council
Electric Power Research Institute
J. Paul Getty Conservation
Institute
Southern California Edison Company

SPONSORS AND DONORS

Environmental Engineering Science

Government Sponsored Projects

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of Los Angeles County

State

California Air Resources Board

Federal

Department of Defense
Department of Energy
Environmental Protection Agency
Geological Survey
National Institute of Environmental
Health Sciences
National Institutes of Health
National Science Foundation
Office of Naval Research
Public Health Service

Private Sources

Discretionary Funds - General

General Motors

Discretionary Funds - Specific Program Areas

Chemistry Consortium (CIT)
Jessie Smith Noyes
Foundation
Powell Foundation
SURF funds (CIT)

Sponsored Research Projects

Dupont Company
Electric Power Research Institute
Keck Foundation
Pacific Gas and Electric Co.
Southern California Edison Co.

SUMMARIES OF RESEARCH PROJECTS

LIST OF PROJECTS

	<u>Page</u>
A. <u>WATER QUALITY AND AQUATIC CHEMISTRY</u>	27
The Photocatalytic Production of H ₂ O ₂ and Organic Peroxides Mineral Surfaces in Aqueous Suspensions	27
Photochemical Transformation of Chemical Compounds with Quantum-Sized Semiconductor Colloids	29
S(IV), Hydroxyalkylsulfonate and Sulfur Ester Chemistry	31
Catalytic Autoxidation of Chemical Contaminants by Heterogeneous and Homogeneous Transition Metal Complexes	31
Fog and Cloud Chemistry	36
Mechanisms of Mineral Dissolution	38
Surface Chemistry of Iron Oxide (Hematite, α -Fe ₂ O ₃) Colloidal Particles in Aqueous Systems	39
Dynamics of Arsenic and Selenium in Water/Sediment Systems	41
Sorption Kinetics in the Modeling of Hydrophobic Organic Transport in Groundwaters	42
B. <u>APPLIED AND ENVIRONMENTAL BIOLOGY</u>	43
Genetics of Methylotrophic Functions	43
Regulation of Methylotrophic Functions	44
Genetics in Marine Methylotrophs	45
Biochemistry and Genetics of the Particulate Methane Monooxygenase	46
Environmental Degradation of Hydrocarbons by Methanotrophs	47
Physics, Chemistry, and Biology of Virus Transport Through Porous Media	48

	<u>Page</u>
Iron Reduction by <i>Shewanella Putrefaciens</i>	49
Toxicity of Hydrazine Toward Species of Kelp	50
C. <u>ENVIRONMENTAL HYDRAULICS AND COASTAL ENGINEERING</u>	51
Contaminant Transport Processes Between Water and Sediment Beds in Rivers	51
Transport and Dispersion of Small Particles in Groundwater Flow	52
Research Plan for Experimental Deep Ocean Sludge Disposal for Orange County	53
Settling Characteristics of Digested Sewage Sludge Particles	54
Thermal Effects Study at San Onofre Nuclear Generating Station	56
Mechanics of Turbulent Buoyant Jets	57
Fluid Mixing Across Density Interfaces	58
Turbulent Kinetic Energy Dissipation in Plumes	60
Breaking Waves: Their Kinematic Properties and Their Interaction with the Bottom	61
A Study of Tsunamis: Their Generation, Propagation, and Coastal Effects	63
Wave and Current Interactions with a Bottom Trench	65
Modal Analysis of Solitary Waves Forcibly Generated	68
Nonlinear Stability of the Solitary Waves Forcibly Generated	69
The KdV Model with Boundary Forcing	70

	<u>Page</u>
Anti-symmetric Solutions of the Forced KdV Equation	71
Scattering and Diffraction of Solitary Waves by a Vertical Cylinder	72
Theoretical and Experimental Studies of the Forced Generation of Precursor Solitons	73
Generation and Propagation of Internal Solitary Waves	74
Precursor Solitons Generated by Three-dimensional Disturbances Moving in a Channel	75
Generation and Propagation of Nonlinear Water Waves in a Channel with Variable Cross Section	76
Standing Wave Solutions of the Generalized Boussinesq Model	77
D. <u>AIR QUALITY, ATMOSPHERIC CHEMISTRY AND AEROSOL PHYSICS</u>	79
Protection of Works of Art from Damage Due to Airborne Particulate Matter	79
Protection of Works of Art from Damage Due to Photochemical Smog	81
Acquisition of Acid Vapor and Aerosol Concentration Data in the South Coast Air Basin	83
Control of the Dry Deposition of Nitrogen-Containing Air Pollutants	85
Studies of Visibility-Reducing Organic Aerosols in the Desert Southwestern United States (SCENES-Origin of Organics Study)	86
Development of Strategies for Visibility Improvement Using an Image Processing-Based Visibility Model	87
Characterization of Organic Aerosols in Source Emissions and in Ambient Air	88

	<u>Page</u>
Modeling of Atmospheric Pollutant Concentrations During the Southern California Air Quality Study	90
Determination of Organic Compounds Present in Airborne Particulate Matter	91
Protection of Works of Art from Damage Due to Atmospheric Nitric Acid	92
Validity of Current Aerosol Models for Calculating Gas-Aerosol Equilibrium, Water Content and Size Distributions, and Relative Contributions of Various Source Types to Visibility	93
Optimal Strategies for Air Pollution Control	94
Control of Atmospheric Aerosol Nitrate and Nitric Acid Concentrations	95
Formation and Growth of Aerosols in Atmospheric Photochemistry	96
Studies of Thermodynamics, Transport, and Reaction Processes in Aerosol Particles	98
Scanning of Mobility Spectrometer	101
Dynamics of Aggregate Aerosols	101
Transformations of Inorganic Coal Constituents in Combustion Systems	102
Combustion of Calcium Exchanged Coals	103
Kinetics of Coal Char Combustion	105
Smog Chamber Studies of Hydrocarbon Oxidation and Aerosol Formation	107
Inorganic Constituents of Urban Air Pollution Aerosols	108
Development of a State-of-the-Art Urban Acid Deposition Model	109
Mathematical Modeling of Chemically-Reacting Plumes	110

	<u>Page</u>
E. <u>RISK ASSESSMENT AND REGULATION</u>	111
Risk Assessment in the Nuclear Power Industries	112
Common Knowledge in Models of Information Aggregation and Learning	113

A. WATER QUALITY AND AQUATIC CHEMISTRY

THE PHOTOCATALYTIC PRODUCTION OF H₂O₂ AND ORGANIC PEROXIDES ON MINERAL SURFACES IN AQUEOUS SUSPENSIONS

Investigators: Claudio Kormann*, German Mills, Amy Hoffman*, Michael R. Hoffmann

Support: U. S. Environmental Protection Agency

The formation of H₂O₂ and organic peroxides in illuminated aqueous suspensions of ZnO, TiO₂, and desert sand in the presence of O₂ and organic electron donors is being investigated. In preliminary work, the photocatalytic rate of formation of H₂O₂ on ZnO was shown to depend on the O₂ partial pressure, on the concentration of organic electron donors, and on the concentration of H₂O₂. During the initial phase of irradiation the rate production of H₂O₂ is given by

$$\frac{d [H_2O_2]}{dt} = (\Phi_0 - \Phi_1[H_2O_2]) \cdot (d [hv]_{abs}/dt)$$

where Φ_0 is the quantum yield for H₂O₂ formation, Φ_1 is the quantum yield for H₂O₂ degradation, and $d[hv]_{abs}/dt$ is the photon flux. Steady-state concentrations of H₂O₂ in excess of 100 μM were obtained in illuminated suspensions of ZnO. In the case of ZnO, the quantum yield for H₂O₂ formation, Φ_0 , approached 15% at 330 nm whereas the photodegradation reactions were relatively inefficient. On the other hand, Φ_0 for TiO₂ (1% at 330 nm) was found to be an order of magnitude less than the value for ZnO. Φ_0 for a sample of desert sand (Death Valley, CA) was found to be 10⁻⁴. Photooxidation of acetate and other organic electron donors on colloidal ZnO has been shown to produce substantial concentrations of organic peroxides, ROOH. Illumination of ZnO suspensions containing acetate produced greater than 40% of the measured total peroxide (H₂O₂ & ROOH) as ROOH. These heterogeneous photochemical pathways can be shown to be viable sources of hydrogen peroxide in atmospheric water droplets.

Present research is focused on the detailed mechanisms for the formation of peroxides. Some of the reaction pathways that have been identified include a 2-electron reduction of adsorbed oxygen by conduction band electrons, hydroxyl radical recombination on the particle surface and in the electrical double layer, carbon-centered radical reactions in the bulk aqueous phase, and the homogeneous self-reaction of superoxide. Laser flash photolysis is being used to study the details of surficial electron transfer that leads to peroxide production.

This research is relevant to the production of hydrogen peroxide in natural waters.

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PHOTOCHEMICAL TRANSFORMATION OF CHEMICAL COMPOUNDS WITH QUANTUM-SIZED SEMICONDUCTOR COLLOIDS

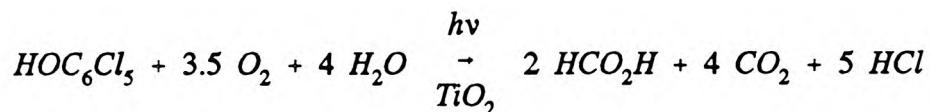
Investigators: Claudio Kormann*, Amy Hoffman*, German Mills,
Michael R. Hoffmann

Support: U. S. Environmental Protection Agency, DuPont Company

The syntheses of transparent colloidal solutions of extremely small titanium dioxide, cadmium sulfide, copper oxide and zinc oxide particles ($d < 3 \text{ nm}$) in water, ethanol, 2-propanol, and acetonitrile have been achieved. Quantum-size effects are observed during particle growth and at the final stages of synthesis. These effects have been interpreted using a quantum-mechanical model.

Semiconductors such as ZnO , TiO_2 , Fe_2O_3 and CdS are known to be suitable photochemical catalysts for a wide variety of reactions. When an incident photon with an energy of $h\nu$ matches or exceeds the bandgap-energy of the semiconductor an electron is promoted from the valence band into the conduction band leaving a hole behind in the valence band. Electrons and holes can then recombine (and dissipate the input energy as heat) or, in the case of Q-size particles, they can migrate to the surface and be trapped in surface states. The local electric field near the surface of a bulk semiconductor electrode results in the separation of the oppositely charged e_{cb}^- and h_{vb}^+ . The hole at the interface can accept an electron from a surface-bound hydroxyl group to form a surface bound hydroxyl radical.

In our laboratory we have recently achieved the complete degradation of pentachlorophenol using various semiconductor particles as photocatalysts with the following stoichiometry:



The oxidation proceeds OH radical attack resulting in the total destruction of PCP. In a similar fashion we have studied the complete photodegradation of chloroform, CHCl_3 , on TiO_2 particles to produce Cl^- , H^+ , and CO_2 as the only products within 15 minutes. These studies show that Q-size semiconductor colloids are effective photocatalysts for the elimination of undesirable chemical contaminants from water.

In a related study we have investigated the capability of Q-sized colloids to initiate polymer formation (e.g. polymethylmethacrylate, poly-methyl acrylate, polystyrene) in irradiated suspensions of ZnO , TiO_2 and CdS . Polymers were formed from their corresponding monomers in high yields with average molecular weights varying from 1×10^6 to 1.5×10^6 Daltons and with quantum yields, Φ , ranging from 8 to 40.

In another recent study we have investigated the kinetics and mechanism of the photo-assisted autoxidation of S(IV) in aqueous colloidal suspensions of α -Fe₂O₃ have been studied over the Ph range of 2 to 10.5. Similar kinetic behavior toward S(IV) was observed for colloidal suspensions of TiO₂. Quantum yields, ϕ , ranged from 0.08 to 0.3 with a maximum yield found at Ph 5.7. Upon band-gap illumination conduction-band electrons and valence-band holes are separated; the trapped electrons are transferred either to surface bound dioxygen or to Fe(III) sites on or near the surface while the trapped holes accept electrons from adsorbed S(IV) to produce S(V). The formation of S(V) radicals indicates that the reaction proceeds via successive one-electron transfers. The relatively high quantum yields are attributed in part to the desorption of SO₃⁻ from the particle surface and subsequent initiation of a homogeneous free radical chain autoxidation of S(IV) to S(VI).

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S(IV), HYDROXYALKYLSULFONATE AND SULFATE ESTER CHEMISTRY

Investigators: Terese M. Olson*, Martha Conklin*, Fangdong Yin**, Jochen Kraft, Eric A. Betterton, Michael R. Hoffmann

Support: U. S. Environmental Protection Agency, Electric Power Research Institute, and the National Institute of Environmental Health Sciences

Kinetic and thermodynamic data have obtained for the addition of S(IV) to benzaldehyde, glyoxal, methylglyoxal, acetaldehyde, hydroxyacetaldehyde, and glyoxylic acid. This data has been used to predict the relative effectiveness of the corresponding hydroxylalkylsulfonates as reservoirs for S(IV) in atmospheric water droplets. A linear-free-energy relationship between hydroxylalkylsulfonate stabilities and carbonyl hydration constants has been developed to estimate the stability constants of other unknown carbonyl-bisulfite adducts. Formation rates of at least four of the adducts studied were greater than or comparable to the formation rate of α -hydroxymethanesulfonate (HMS). Under most fog- and cloud-water conditions, we have shown that these rates are slower than gas transfer processes. Equilibrium calculations in an open atmosphere indicate that hydroxy- acetaldehyde, glyoxal, glyoxylic acid, and to a smaller extent, methylglyoxal, lead to potentially significant enrichment of S(IV) in the liquid phase, although HMS is an even better reservoir for S(IV). Scavenging of SO_2 from the gas-phase due to hydroxylalkylsulfonate formation becomes important at high liquid water contents, Ph 3 \geq 5, and when an excess partial pressure of the aldehyde is present. The overall dissolution of RCHO and SO_2 into a droplet and the subsequent formation of the hydroxylalkylsulfonate, also results in a net increase in acidity, which in a weakly buffered solution, can be more than a unit drop in Ph.

We have shown also that transition metal ions such as Fe(III), Cu(II), Co(II), Co(III), and Mn(II) are effective homogeneous catalysts for the autoxidation of sulfur dioxide in aqueous solution. Fe(III) and Mn(II) are the most effective catalysts at ambient concentrations for the catalytic autoxidation of S(IV) to S(VI) in cloud- and fogwater. Mechanisms for the homogeneous catalysis by Fe(III) and Mn(II) that have been developed include a free radical chain mechanism, a polar mechanism involving inner-sphere complexation followed by a two-electron transfer from S(IV) to bound dioxygen, and photo-assisted electron transfer.

Current research has been focused on a study of the kinetics, thermodynamics and mechanisms of the formation and hydrolysis of sulfate esters such as CHOSO_3H and $(\text{CH}_3\text{O})_2\text{SO}_2$ in cloudwater. Sulfate esters arise from the oxidation of S(IV) by organic peroxides, ROOH, and by the esterification of sulfuric acid with alcohols such as methanol. A knowledge of these reaction pathways will be vital to the complete assessment of methanol as a viable alternative to gasoline as a fuel for automobiles in highly polluted urban environments.

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CATALYTIC AUTOXIDATION OF CHEMICAL CONTAMINANTS BY HETEROGENEOUS AND HOMOGENEOUS TRANSITION METAL COMPLEXES

Investigators: Andrew P. Hong*, Kenneth P. Leung**,
Natasha Kotronarou**, Michael R. Hoffmann

Support: U. S. Environmental Protection Agency, County
Sanitation Districts of Los Angeles County

Heterogeneous and homogeneous metal phthalocyanine complexes have been shown to be effective catalysts for the aqueous-phase autoxidation of hydrazine, hydrogen sulfide, sulfur dioxide, and thiols under neutral and alkaline conditions. The heterogeneous catalysts exhibited longer catalytic lifetimes than their homogeneous analogs for the autoxidation of reductants. However, the attachment of the reactive complexes to solid supports such as silica gel and polystyrene resulted in reduced catalytic activity. This was attributed to diffusion limitations within the internal pores of the solid support. The relative efficiency of the various catalysts, which are linked to the surface either through direct complexation of the metal center or through covalent bonding of a peripheral group on the macrocyclic ligand, follows a trend that reflects the relative capacity of the hybrid complexes to activate molecular oxygen. This ability depends on the nature of the complexing ligand located trans to dioxygen. Both homogeneous and heterogeneous transition-metal catalysis may offer a potential method for tertiary pollution control.

In an on-going study, the effectiveness of these catalysts has been demonstrated for the control of hydrogen sulfide in wastewater transport and treatment systems.

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FOG AND CLOUD CHEMISTRY

Investigators: J. William Munger*, Jeff Collett*, Bruce Daube,
Michael R. Hoffmann

Support: California Air Resources Board

The aerosol at elevated sites in the Los Angeles basin is a mixture of sea salt and pollution-derived secondary aerosol. The influence of sea salt declines with increasing distance from the coast. Nitric acid appears to react with the NaCl in sea-salt aerosol to release HCl and form NaNO_3 in the aerosol. At inland sites aerosol concentrations differ during the day when the onshore flow transports pollutants to the sites, while lower concentrations were observed at night when drainage flows from nearby mountains influenced the sites. Variations in liquid water content are a major influence on cloudwater concentration.

Comparisons of the ionic concentrations in two size-segregated fractions collected during each sampling interval suggest that there is a large difference between the average composition of the smaller droplets and that of the larger droplets. For each time interval, the concentration of Na^+ , Ca^{2+} and Mg^{2+} in the large droplet fraction was observed to be higher than in the small droplet fraction. The concentrations of SO_4^{2-} , NO_3^- , NH_4^+ , and H^+ were higher in the small droplet fraction. Chloride concentrations were nearly equal in both fractions. Differences in the composition of size-fractionated cloudwater samples suggest that large droplets are formed from sea salt and soil dust, which are large aerosol, and small droplets are formed on small secondary aerosol composed of primarily ammonium sulfate and ammonium nitrate. The concentrations of several components that exist partly in the gas phase (e.g. Cl^- , HCOOH , and CH_3COOH) appear to be independent of droplet size.

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MECHANISMS OF MINERAL DISSOLUTION

Investigators: Bernhard Wehrli*, James J. Morgan

Support: Andrew W. Mellon Foundation, EAWAG (Swiss Federal Institute for Water Resources and Water Pollution Control)

Chemical weathering of minerals controls the neutralization of acid rain. As a consequence, the concentration of dissolved aluminum has risen in sensitive aquatic environments to toxic levels. Mechanistic models on a molecular scale are essential for a general understanding of the kinetics of weathering processes. The dissolution reaction involves a change in the first coordination sphere of metal ions - a fact which can be modelled in terms of lattice statistical nearest-neighbor relations. Monte Carlo simulations have been performed in order to clarify the interdependence between surface geometry and dissolution kinetics. The model predicts that the "roughness" of a dissolved oxide surface is a simple function of the activation energy of the process.

An experimental study on the dissolution of $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{OH}_2)_{12}^{7+}$ is in progress. This polynuclear complex can be identified by $^{27}\text{AL-NMR}$ and serves as a structurally well-characterized model compound. The kinetic data can be used to test and calibrate a lattice statistical model. The results are expected to close a gap in the knowledge on the kinetics of Al(III) in the aqueous environment.

Publication:

Wehrli, B., "Monte Carlo Simulations of Surface Morphologies during Mineral Dissolution," *J. Colloid Interface Sci.*, 132, 230-241, 1989.

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SURFACE CHEMISTRY OF IRON OXIDE (HEMATITE, α -Fe₂O₃) COLLOIDAL PARTICLES IN AQUEOUS SYSTEMS

Investigators: Liyuan Liang*, James J. Morgan

Support: Jessie Smith Noyes Foundation, Andrew W. Mellon Foundation

Particles in the colloidal size range are of great interest in environmental science and engineering. Aqueous oxide particles have high specific surface areas, adsorb ions and molecules from water, and may remain kinetically stable in an aqueous phase with respect to coagulation. A key to understanding particle stability and coagulation is the surface chemistry of those solutes which strongly influence electrostatic forces between particles. Experiments using submicron hematite particles (α -Fe₂O₃, 75nm in diameter) reveal important features of coagulation dynamics through light scattering measurements, electrokinetic measurements of electrical charge on oxide particles, and adsorption measurements for surface species. Acid-base titration data indicate that the zero-charge Ph of colloidal hematite is 8.5, in agreement with electrophoretic mobility measurements.

In the presence of non-specifically adsorbed ions (e.g., Na⁺), the coagulation of colloidal hematite is achieved by compression of the diffuse ionic layer. Specifically adsorbed ions (e.g., phosphate) dramatically reduce surface charge of Fe₂O₃ particles. For inorganic solutes the order of effectiveness in achieving hematite coagulation is:

anions: phosphate > sulphate > chloride

cations: magnesium > calcium > sodium ~ potassium

Adsorption studies reveal that phthalate ions specifically adsorb, and that the process is due to carboxylic group bonding to the surface. Hematite coagulation rates in the presence of poly-aspartic acid (PAA) reveal that the polyelectrolyte is unusually effective in coagulation. Similar coagulation features are observed when naturally occurring organics (e.g., fulvic and humic acid from Suwannee River) are used. Adsorption of long-chain fatty acids (C₈ to C₁₂) can be interpreted in terms of the total energy contributed by electrostatic, hydrophobic and specific chemical interactions. Coagulation rates of hematite with respect to fatty acid concentration show systematic variations with chain length (hydrophobic effect). The results of the laboratory findings prove useful in explaining field observations on iron particle behavior in lakes, rivers and estuaries.

Publications:

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DYNAMICS OF ARSENIC AND SELENIUM IN WATER/SEDIMENT SYSTEMS

Investigators: Michael J. Scott*, James J. Morgan

Support Andrew W. Mellon Foundation, William and Flora Hewlett Foundation, UC Water Resources Center

Arsenic and selenium are naturally-occurring, non-metallic elements with complex chemical and biological behavior in aquatic environments. Contamination of Kesterson Reservoir (California) is a well-known example of selenium accumulation in ecosystem water/sediments. Arsenic and selenium can both exist as inorganic oxyanions (e.g., arsenite, arsenate; selenite, selenate) in water. Adsorption to oxide mineral surfaces, e.g., iron oxides or manganese oxides, is an important process regulating the aqueous concentrations of arsenic and selenium species in water. Thermodynamic models predict that arsenate and selenate, AsO_4^{3-} and SeO_4^{2-} , respectively, are the stable forms in oxygen-containing waters, while arsenite and selenite, AsO_3^{3-} and SeO_3^{2-} , respectively, are stable in anoxic waters.

Environmental observations for these elements strongly suggest that chemical transformations between reduced and oxidized forms are quite slow, that many systems are far from equilibrium, and that kinetic information is needed, in addition to thermodynamic data, to predict actual behavior in natural systems. This research addresses several key questions; among them, what chemical reactions control the geochemical distribution of arsenic and selenium in contaminated aquatic systems, and what is the role of metal oxide surfaces in the rates of transformation under environmental conditions? Laboratory experiments with the iron(III) oxide goethite ($\alpha\text{-FeOOH}$) and the manganese(IV) oxide birnessite ($\delta\text{-MnO}_2$) are investigating rates of adsorption and rates of oxidation of reduced arsenic and selenium species under a wide range of pH, temperature, and ionic compositions relevant to natural conditions. The product of this research will include rate expressions for adsorption and redox reactions of arsenic and selenium at iron and manganese oxide surfaces.

Publication:

Scott, M. J., Morgan, J. J., "Energetics and Conservative Properties of Redox Systems," in Chemical Modeling of Aqueous Systems II. D. C. Melchior and R. L. Bassett, Eds., ACS, Washington, D.C., pp. 368-378, 1989.

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SORPTION KINETICS IN THE MODELING OF HYDROPHOBIC ORGANIC TRANSPORT IN GROUNDWATERS

Investigators: Mark Schlautman*, James J. Morgan, Norman H. Brooks

Support: Andrew W. Mellon Foundation, William and Flora Hewlett Foundation

Understanding sorption processes is an important key to describing the fate of hydrophobic organic pollutants in groundwaters. Sorption can significantly alter the physical transport and chemical reactivity of these compounds. Transport and reaction will determine whether treatment methods utilized in the remediation of polluted aquifers can succeed. Existing models attempt to describe the sorption process on fixed soil particles. These models simulate sorption as either an equilibrium process or nonequilibrium process coupled with the classical convective-dispersive transport equation. In this study, attempts are being made to determine the conditions under which results from these two types of models converge. This information will be useful in remediation efforts since the amount of equilibrium data and correlations vastly exceeds the kinetic data for sorption processes.

In addition, the importance of sorption to mobile, colloid-sized particles is being examined. Colloid transport may be a significant mechanism for hydrophobic organic pollutants in an aquifer. Little information is available on the role of particle transport in the fate of these compounds. A comprehensive groundwater model incorporating both solute and particle transport and sorption onto migrating particles as well as onto the soil matrix is needed to adequately predict the movement of organics at certain polluted sites.

This is a preliminary report of work in progress, and as yet no written reports are available for distribution.

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B. APPLIED AND ENVIRONMENTAL BIOLOGY

GENETICS OF METHYLOTROPHIC FUNCTIONS

Investigators: Christina Morris, Louis Boschelli*, Michael Kuhn,
Mary E. Lidstrom

Support: Department of Energy

Bacteria capable of growth on methane or methanol (methylo-trophs) have strong commercial potential in the area of hydrocarbon catalysis, due to unique oxidative functions associated with methylo-trophic growth. In order to understand and exploit these functions, it is necessary to carry out basic studies of gene organization and expression in these bacteria. We have initiated genetic studies in methylo-trophs by isolating and characterizing genes necessary for the oxidation of methanol. We have shown that in one methanol-utilizing strain, this system requires at least 17 gene functions. Several of these functions have been identified by characterizing mutants deficient in these genes and by expressing the genes in an alternate host (*Escherichia coli*). We have shown that the genes encoding some of these functions are conserved amongst a variety of methylo-trophic bacteria, and we have used this similarity to isolate methanol oxidation genes from methane-oxidizing bacteria. We are currently cloning and characterizing promoter regions from these genes in order to determine the molecular basis for regulation of each, and a putative consensus promoter sequence has been identified from these studies.

Publications:

Anderson, D. J., Lidstrom, M. E., "The moxFG Region of *Methylobacterium* AM1 Encodes Four Mox Proteins." *J. Bacteriol.*, 170, 2254-2262, 1988.

Anderson, D. J., Morris, C. J., Nunn, D. N., Anthony, C., Lidstrom, M. E., "Nucleotide sequence of the *Methylobacterium extorquens* sp. AM1 moxF and J genes involved in methanol oxidation", submitted to Gene.

*Graduate Student, Chemical Engineering

REGULATION OF METHYLOTROPHIC FUNCTIONS

Investigators: Peggy Arps, Cinder Krema-DiSpirito*, Eun Lee,
Mary E. Lidstrom

Support: National Institutes of Health

Bacteria that grow on methane or methanol (methylo trophs) play a key role in maintaining a healthy environment. Not only are they an essential link in the global carbon cycle, they also detoxify hydrocarbons and are ubiquitous in aerobic habitats. In order to understand and manipulate the natural activities of these bacteria, it is essential to study the regulation of methylotrophic activities at both the whole cell and molecular levels. We have carried out studies of methylotrophic activities in both methanol and methane utilizing strains. These studies have focused on the methanol oxidation system. We have determined the functions of 10 of the 17 known methanol oxidation (Mox) genes, and we are now attempting to determine which of the other 7 are involved in regulation. In addition, we have screened 150 new Mox mutants to determine whether any additional genes are present. Future studies will involve growing cells in continuous culture and testing the effects of changing environmental parameters on the gene products of interest. In this way we will determine the cellular level(s) at which regulation of gene expression occurs.

Publications:

Stephens, R. L., Haygood, M. G., Lidstrom, M. E., "Identification of Putative Methanol Dehydrogenase (moxF) Structural Genes in Methylo trophs and Cloning of moxF Genes from *Methylococcus capsulatus* Bath and *Methylomonas albus* BG8," *J. Bacteriol.*, 170, 2063-2069, 1988.

Kim, Y. M., Lidstrom, M. E., "Plasmid Analysis in Pink Facultative Methylotrophic Bacteria Using a Modified Acetone-Alkaline Hydrolysis Method," *FEMS Microbiol. Lett.* 60, 125-130, 1989.

Krema-DiSpirito, C., Lidstrom, M. E., "Hydroxypyruvate Reductase from *Methylobacterium extorquens* AM1," *Meth. Enzym.* 188, in press.

Arps, P. J., Kim, Y. M., Lidstrom, M. E., "Mox A Genes from Methanotrophic Bacteria," submitted to *J. Bacteriol.*

*Graduate Student, Environmental Engineering Science

GENETICS IN MARINE METHYLOTROPHS

Investigators: Alan A. DiSpirito, Daryle Waechter-Brulla,
Mary E. Lidstrom

Support: Office of Naval Research

Genetics in marine bacteria has not been studied in detail, and in order to pursue problems concerning bacteria in marine and estuarine environments, it is essential to develop basic information concerning gene organization, expression and manipulation in marine strains. We have isolated and characterized an unusual marine bacterium, a *Methylomonas* strain that grows extremely well on methane or methanol. This bacterium came from an enrichment of samples from the Hyperion sewage outfall, near Los Angeles, and shows a number of qualities that make it interesting from a genetic and commercial point of view. We have initiated studies of this bacterium by concentrating on the methanol oxidation system. The methanol dehydrogenase and the cytochromes involved in methanol oxidation have been purified and characterized, and two methanol oxidation genes, those encoding the structural protein of the methanol dehydrogenase and one necessary for positioning the methanol dehydrogenase cofactor, have been cloned and characterized. We are now cloning and characterizing the promoter regions for these genes, in order to determine molecular mechanisms of regulation. Collaborations have also been carried out with Jon Sieburth (University of Rhode Island) and Colleen Cavanaugh (Harvard University) to study and characterize other marine methanotrophs.

Publications:

DiSpirito, A. A., Lipscomb, J. D., Lidstrom, M. E., "Soluble Cytochromes from the Marine Methanotroph, *Methylomonas* A4," submitted to J. Bacteriol.

Lidstrom, M. E., "Isolation and Characterization of Marine Methanotrophs," Antonie van Leeuwenhoek J. Microbiol., 54, 189-199, 1988.

Cavanaugh, C. M., Levering, P. R., Maki, J. S., Mitchell, R., Lidstrom, M. E., "Symbiosis of Methylotrophic Bacteria and Deep Sea Mussels," Nature, 325, 346-348, 1987.

Sieburth, J. M., Johnson, P. W., Eberhardt, J. A., Sieracki, M. E., Lidstrom, M., Laux, D., "The First Methane-oxidizing Bacterium from the Upper Mixing Layer of the Deep Ocean: *Methylomonas pelagica* sp nov," Current Microbiology, 14, 285-293, 1987.

BIOCHEMISTRY AND GENETICS OF THE PARTICULATE METHANE MONOOXYGENASE

Investigators: Andrew Shiemke, Brenda Speer, Alan A. DiSpirito,
Mary E. Lidstrom

Support: National Institutes of Health

Bacteria that grow on methane (methanotrophs) contain an enzyme that oxidizes methane to methanol, known as the methane monooxygenase (MMO). Recent evidence has shown that two forms of the MMO exist in some strains, one soluble (sMMO) with a broad substrate specificity and one particulate (pMMO), with a more narrow substrate specificity. Although the sMMO has been purified and characterized from three strains, the pMMO is extremely unstable and has not yet been purified. However, this form of the enzyme appears to be the most common, and is probably the form expressed in nature. In order to utilize the detoxification capabilities of these bacteria for *in situ* remediation, it is necessary to characterize the pMMO system and determine its expression *in situ*. This project has approached the pMMO with a combination of biochemical and genetic studies. In the biochemical studies, we have shown that copper, known to be necessary for the expression of the pMMO, also stabilizes the activity in cell-free extract, and have correlated activity of the pMMO with an unusual copper-EPR signal. Future work will concentrate on characterization of the copper-EPR signal, and purification of the protein complex responsible for the signal. For the genetic approach, we have purified the small acetylene-binding protein which is assumed to be part of the pMMO. We have generated N-terminal amino acid sequence and have used a synthetic oligonucleotide probe based on that sequence for hybridization experiments with genomic blots. Preliminary results suggest that specific sequences hybridize, and we are in the process of cloning the gene encoding this polypeptide. Future work will focus on the cloning and characterization of all detectable pMMO genes.

This is a preliminary report of work in progress, and as yet no written reports are available for distribution.

ENVIRONMENTAL DEGRADATION OF HYDROCARBONS BY METHANOTROPHS

Investigators: Jeremy Semrau*, Mary E. Lidstrom

Support: Department of Defense

Bacteria that grow on methane (methanotrophs) are capable of cooxidizing a variety of hydrocarbons, including halogenated ethanes and methanes. Some of these compounds, for instance trichloroethylene (TCE) are toxic pollutants that are particularly recalcitrant in aquatic and terrestrial systems. Recent evidence suggests that it may be possible to increase *in situ* degradation rates for these compounds by injecting natural gas into the contaminated systems. In order to define and utilize these natural activities of methanotrophs, it is necessary to study the kinetics, biochemistry and genetics of the systems that carry out the cooxidation reactions. This project has just been initiated, but so far we have shown that kinetic constraints play a key role in determining rates of cooxidation. It may be possible to increase these rates for process development by genetically modifying the host strains, or by transferring the necessary genes to alternate strains.

Publication:

Little, C. C., Palumbo, A. V., Herbes, S. E., Lidstrom, M. E., Tyndall, R. L., Gilmer, P. J., "Trichloroethylene biodegradation by a methane-oxidizing bacterium," *Appl. Environ. Microbiol.* 54, 951-956, 1988.

*Graduate Student, Environmental Engineering Science

PHYSICS, CHEMISTRY, AND BIOLOGY OF VIRUS TRANSPORT THROUGH POROUS MEDIA

Investigators: Stanley Grant*, Mary Lidstrom, John List

Support: Andrew W. Mellon Foundation, National Institutes of Health

The goal of this project is to identify the dominant physical, chemical and biological factors affecting dispersal of viruses in soil and groundwater environments, and to develop transport models that can be utilized in risk assessment. Gene probe assays of viral DNA are currently being tested as a way of measuring the concentration of total (i.e. viable and inactivated) viruses present in a fluid sample. Coupled with the conventional Plaque Forming Unit (PFU) assay, the gene probe assay should allow, for the first time, a distinction to be made between virus inactivation and irreversible virus attachment to grain surfaces in transport experiments.

The new assay techniques described above will be used to study the nature of virus attachment (and detachment) to quartz sand as a function of pH and ionic strength. Electrostatic charge on the grain and virus surfaces, as measured by electrophoretic mobility, will be correlated to the rate, extent and reversibility of virus attachment to grain surfaces. Knowledge gained from these experiments will be incorporated into a mathematical model of virus inactivation, advection and dispersion. Column experiments will be performed to evaluate the performance of the model and measure deposition flux under favorable attachment conditions.

This is a preliminary report of work in progress and as yet no written reports are available for distribution.

*Graduate Student, Environmental Engineering Science

IRON REDUCTION BY *SHEWANELLA PUTREFACIENS*

Investigators: Thomas J. DiChristina*, Mary E. Lidstrom

Support: Charles Lee Powell Foundation, Andrew W. Mellon Foundation

The ability of the marine bacterium, *Shewanella putrefaciens* to utilize iron as a terminal electron acceptor was studied using both biochemical and genetic approaches. Large scale culture in a biostat system was used to show that iron reduction does occur via an electron transport chain, and that it can occur concurrently with nitrate reduction but not concurrently with aerobic respiration. A plate screening method was developed and used to isolate a series of mutants generated by both chemical and transposon-mediated mutagenesis. These mutants were characterized according to their cytochrome profile and their iron reduction ability. In order to characterize these mutants genetically, a broad host-range cloning system was developed for this strain using the vector pVK100, a clone bank was constructed, and the mutants were complemented with clones from the bank. A microtiter screening method was used to identify complementing clones. Preliminary analysis of the clones showed that at least three genetic classes of mutants were present.

*Graduate Student, Environmental Engineering Science

TOXICITY OF HYDRAZINE TOWARD SPECIES OF KELP

Investigators: David E. James*, Wheeler J. North

Support: Pacific Gas and Electric Company, Keck Foundation, William and Flora Hewlett Foundation

A bioassay system was developed using microscopic stages (gametophytes) of various kelp species as test organisms. These tiny plants consist of only a few cells when they are used in our system. They metabolize and grow rapidly during this part of the life cycle. We can thus determine responses to toxicants in relative short time periods (i.e., a few days). Furthermore, kelps are important ecologically in nearshore marine communities. They create forest-like habitat, provide shelter for fishes, and settling substrate and food for many invertebrates. Consequently there is considerable interest in possible effects from discharged wastewaters or the components thereof. Our study focused primarily on toxicity of hydrazine, a chemical found in effluents from nuclear power plants (hydrazine is added to boiler water to control scale formation and is discharged when water in a boiler is replaced). We evaluated toxicity thresholds to hydrazine for seven species of kelp gametophytes found in coastal California waters. We also used our bioassay system to evaluate toxicity of deep water sediments off Palos Verdes, provided by the Los Angeles County Sanitation Districts.

Publications:

James, D. E., "Effects of Hydrazine and Other Toxicants on Early Life Stages of California Brown Algae," Ph.D. thesis, California Institute of Technology, December 1988.

North, W. J., "Review of *Macrocystis* Biology," An Introduction to Applied Phycology; I, Akatsuka, ed., Hydrobiologia. Dr. W. Junk Publishers, Dordrecht, in press.

*Graduate Student, Environmental Engineering Science

C. ENVIRONMENTAL HYDRAULICS AND COASTAL ENGINEERING

CONTAMINANT TRANSPORT PROCESSES BETWEEN WATER AND SEDIMENT BEDS IN RIVERS

Investigators: Alexander Elliott*, Norman H. Brooks, James J. Morgan,
Robert C. Y. Koh

Support: U.S. Geological Survey, Andrew W. Mellon Foundation,
Walter L. and Reta Mae Moore Fellowship

Toxic contaminant transport in natural rivers involves exchange processes between the stream flow and the sediment bed. The sediment beds and banks of a river can act as the storage place for contaminants dumped into a river system. There are two basic cases, the transport into the bed (capture) and out of the bed (release). These are both non-equilibrium situations where the chemical and physical processes both may govern the rate of capture and release. Computer models for predicting toxics concentrations in river systems are limited by the accuracy of the representation of the exchange processes between the bed and the water column.

The purpose of this research project is to investigate the fundamentals of bed-exchange of adsorbing and non-adsorbing inorganic tracers, a 5-meter long recirculating laboratory flume with a fine sand bed. A typical flume experiment is started with clear water flowing over a sand bed, often with ripples; then a measured dose of tracer is added quickly in the open channel flow. Depth profiles of tracer concentration in pore water in the sand bed are then measured at various times, as well as the concentration in the channel flow. So far experimental procedures have been developed and results have been obtained to describe quantitatively the physical processes of exchange of a non-adsorbing, conservative tracer. It has been found that bed forms (ripples) cause significant percolation into and out of the bed locally due to the variation of pressure on the top of the sand bed.

The results of the research will be utilized by other environmental researchers, and by environmental engineers predicting and controlling river pollution problems involving bed exchange.

This is a preliminary report of work in progress, and as yet no written reports are available for distribution.

*Graduate Student, Environmental Engineering Science

TRANSPORT AND DISPERSION OF SMALL PARTICLES IN GROUNDWATER FLOW

Investigators: Russell Mau*, Norman H. Brooks, James J. Morgan,
Robert C. Y. Koh

Support: Andrew W. Mellon Foundation

Trace contaminants sometimes have larger than expected mobility in ground-water systems because of adsorption onto small natural particles ($< 10 \mu\text{m}$) which are carried through the porous medium. In this case adsorption onto solid surfaces (of the small particle) does not immobilize a contaminant as presumed in almost all contaminant transport models. Therefore, an understanding of transport of contaminants depends on knowledge of both the particle behavior in ground-water flow and the adsorption equilibria and kinetics for the contaminant onto the solids.

The objectives of this research are: (1) to complete an experimental study of small particle transport in porous media, which is now in progress; (2) conduct experiments on the transport of selected contaminants (metal ions) together with colloids in water flow through sand in a packed column; and (3) continue development of appropriate mathematical models.

Colloid suspensions in water with or without a contaminant (metal ions, such as lead) are made to flow through sand columns at rates representative of natural ground-water flow. The behavior of the concentration front (breakthrough curve) provides the data necessary to determine particle velocity and dispersion from the advective-diffusion equation (with filtration term also included). The filter coefficient is determined from the steady-state plateau of concentration of colloids reached at the distance of the sampling port. Similar properties will be measured for the contaminant breakthrough in simultaneous or separate experiments. The concentration of particles in small samples, withdrawn from a position near the base of the column at various times, is determined by measuring turbidity (intensity of light scattering) or fluorescence. The contaminant concentrations on the colloids and in suspension are measured by usual centrifuge and extraction procedures.

The effect of the following variables on particle and contaminant behavior will be investigated: (1) flow rate; (2) particle size; (3) media grain size; (4) system pH; (5) system ionic strength; and (6) surface chemistry of the solids.

This is a preliminary report of work in progress, and as yet no written reports are available for distribution.

*Graduate Student, Environmental Engineering Science

RESEARCH PLAN FOR EXPERIMENTAL DEEP OCEAN SLUDGE DISPOSAL FOR ORANGE COUNTY

Investigators: Norman H. Brooks, Robert C. Y. Koh, Robert G. Arnold*

Support: Sanitation Districts of Orange County, National Oceanic and Atmospheric Administration, Andrew W. Mellon Foundation, William and Flora Hewlett Foundation

The discharge of sewage sludge into the ocean via an outfall is not now permitted. Nonetheless the option may in some cases be more desirable than other disposal options (to land or incineration). Previous studies by EQL have (i) assessed ocean alternatives for the southern California area, and (ii) developed a research plan to show what could be learned with a full-scale experimental sludge discharge of 150 dry tons/day of sludge by the County Sanitation Districts of Orange County into deep water (over 1000 feet). An updated version of the original research plan has been prepared, based on discharge of only half of the sludge solids (75 tons/day) and providing more details on initial plume behavior.

National policy for sludge disposal has taken into account the findings of the above-mentioned EQL studies with regard to ocean disposal of sludge. The 1987 amendments to the Clean Water Act specifically enable EPA to grant a research permit to Orange County for the deep water sludge outfall and the conduct of the developed research plan.

Publications:

Brooks, N. H., Arnold, R. G., Koh, R. C. Y., Jackson, G. A., Faisst, W. K., "Deep Ocean Disposal of Sewage Sludge Off Orange County, California: A Research Plan," EQL Report No. 21, second edition, 1990.

Brooks, N. H., Arnold, R. G., Koh, R. C. Y., Jackson, G. A., Faisst, W. K., "A Research Plan for Deep-Ocean Disposal of Sewage Sludge off Orange County, California," in Oceanic Processes in Marine Pollution, Volume 2, Physiochemical Processes and Wastes in the Ocean, edited by T. P. O'Connor, W. V. Burt, I. W. Duedall, published by Robert E. Krieger, Malabar, Florida, pp. 99-115, 1987.

*Now Assistant Professor at University of Arizona

SETTLING CHARACTERISTICS OF DIGESTED SEWAGE SLUDGE PARTICLES

Investigators: Theresa R. F. Wang*, Robert C. Y. Koh, Norman H. Brooks

Support: Andrew W. Mellon Foundation, William and Flora Hewlett Foundation, National Oceanic and Atmospheric Administration, County Sanitation Districts of Orange County, County Sanitation Districts of Los Angeles County

The fall velocities of sewage or sludge particles govern the fate of such particles. Particles are of significance because most of the toxic substances tend to be associated with the particulates. Measurements of fall velocities of particles by means of conventional settling column experiments are not reliable because both sedimentation and coagulation affect the observed settling column experimental results. A conceptual model including sedimentation, coagulation, and vertical diffusion was postulated to provide an alternate interpretation of observed results which showed, through comparison with experiments, that the simple interpretation of experimental data as a cumulative distribution of fall velocities may be significantly in error.

To overcome these errors, a definitive new experimental procedure has been developed by Theresa Wang for measuring the falling velocity and size distributions of sewage particulates suspended in either effluent or sludge. An in-line holographic system is used to make direct optical observations. Through a combination of single and doubly exposed holograms on high resolution holographic film, both the size and the fall velocity of the particles are measured directly, by means of video reconstruction and computer digitization of images.

As an example of policy implications, the EPA's denial of a waiver from secondary treatment for Boston (and the resulting controversy and delay) was based largely on predictions of sewage particle deposition on the seabed which now appear to be erroneous. Sewage particles settle more slowly and disperse more widely than previously believed because particle coagulation is not significant in the sea water when high dilution outfalls are used.

Publications:

Wang, T. R., Koh, R. C. Y., Brooks, N. H., "Settling Column Measurements of Sewage Sludge," Oceanic Processes in Marine Pollution. Vol. 6. Physical & Chemical Processes: Transport and Transformation, edited by Donald J. Baumgartner and Iver W. Duedall, Krieger Publishing, Malabar, Florida, pp. 121-131, 1990.

Wang, T. R., "Laboratory Analysis of Settling Velocities of Wastewater Particles in Seawater Using Holography," EQL Report No. 27 (Ph.D. thesis), 256 pp., 1988.

Wang, T. R., Koh, R. C. Y., Brooks, N. H., "Laboratory Study of the Settling of Wastewater Particles in an Outfall Plume in Seawater," Proceedings of the International Conference of Physical Modeling of Transport and Dispersion, I.A.H.R., MIT, Cambridge, Massachusetts, pp. 8C.25-8C.30, August 7-10, 1990.

Wang, T. R., Koh, R. C. Y., and Brooks, N. H., "Settling Velocity Measurement of Wastewater Particles Using Holography" and "Laboratory Analyses of Settling Velocities of Wastewater Particles in Seawater," both in preparation for submittal to Environmental Science and Technology, 1990.

*Graduate Student, Environmental Engineering Science

THERMAL EFFECTS STUDY AT SAN ONOFRE NUCLEAR GENERATING STATION

Investigators: Kit Yin Ng*, Robert C. Y. Koh, Norman H. Brooks,
E. John List

Support: Southern California Edison Co.

The San Onofre Nuclear Generating Station (SONGS) Units 2 and 3 employ multiple-port diffusers as discharge structures for their circulating water systems. The original design was based on a hydraulic model study performed in the Keck Hydraulics Laboratory in 1972-73. Comparison of laboratory data and the extensive field measurements at the site show that while the general behavior of mixing in the thermal plume is similar to the laboratory findings, the prototype operation exhibits a more complex plume structure, due to the existence of a small vertical temperature gradient. The mixing induced by the staged diffuser is very effective and often results in a cool surface signature, due to the entrainment of the cooler subsurface water. The thermal regulations were met with ease.

A laboratory investigation was conducted to obtain the detailed plume behavior for generic staged diffusers. It is found that the number of discharge ports do not materially affect the mixing achieved as measured beyond the jet near field provided there is enough depth to establish a two-layer flow. This study is of importance in management of waste heat because the staged diffuser is a very effective outfall design for cooling water discharges in open coastal environments.

Publications:

Ng, K. Y., Koh, R. C. Y, "Behavior of the SONGS Thermal Plume - A Program Report," San Onofre Report on 1985 Data, Marine Environmental Analysis and Interpretation, Southern California Edison Company, 86-RD-26, 1986, pp. 3-1 to 3-54. (Also available as Tech Memo 86-1, W. M. Keck Laboratory of Hydraulics and Water Resources, California Institute of Technology, 1986).

Ng, K. Y., "Thermal Plumes from Staged Multiport Diffusers in Uniform Quiescent Environment," Ph.D. Thesis, California Institute of Technology, 1990. (Also Report KH-R-51 of the Keck Hydraulics Lab.)

Ng, K. Y., Koh, R. C. Y., and Brooks, N. H., "Thermal Plumes from Staged Diffusers into a Uniform Quiescent Environment," Hydraulic Engineering, Proceedings of the 1990 National Conference on Hydraulic Engineering, Sponsored by the American Society of Civil Engineers, edited by Howard H. Chang and Joseph C. Hill, published by ASCE, New York, pp. 8-13, 1990.

*Graduate Student, Environmental Engineering Science

MECHANICS OF TURBULENT BUOYANT JETS

Investigators: Panos Papanicolaou*, E. John List

Support: National Science Foundation

Round turbulent buoyant jets were studied in the laboratory using laser-Doppler anemometry and laser-induced fluorescence concentration measurement.

The results obtained show the development of the jet flow and its transition into a buoyancy-driven plume motion. The steady supply of potential energy available from the density deficiency in the plume fluid maintains the momentum flux growth in the plume. The net effect is an increase in the turbulent transport of both momentum and tracer concentration in such flows. Detailed measurements of turbulent fluctuation intensities show that root-mean-square velocity and concentration scale in the same manner as mean flow quantities, so that relative intensities remain invariant in both jet and plume motions. The power spectral density of temperature fluctuations in buoyant jets shows that the decay is in accordance with theoretical arguments for the inertial-diffusive subrange. It appears that the dissipation of the temperature variance in buoyancy-driven flows may result from buoyancy-generated inertia forces rather than the viscous forces.

Overall, the results show that for engineering purposes the transition from jets to plumes is satisfactorily described by present integral theories.

Publications:

Papanicolaou, P. N., List, E. J., "Statistical and Spectral Properties of Tracer Concentration in Round Buoyant Jets," Int. J. Heat Mass Trans., 30, 2059-2071, 1987.

Papanicolaou, P. N., List, E. J., "An Experimental Investigation of Round Vertical Turbulent Buoyant Jets," J. Fluid Mech., 195, 341-391, 1988.

*Post-doctoral fellow, University of California, San Diego (formerly Graduate Student, Environmental Engineering Science)

FLUID MIXING ACROSS DENSITY INTERFACES

Investigators: Imad Hannoun,* Marco Rasi, H. J. Fernando,***
Greg Sullivan,** Talal Balaa,* E. John List

Support: National Science Foundation, US Geological Survey, State of California Water Resources Center

The mechanics of turbulent mixing across a fluid density interface are being studied experimentally in the laboratory. A 1.5-meter-square glass-walled tank, 3.4 meters deep, is fitted with an internal moveable mesh grid that can be oscillated vertically at a prescribed frequency and stroke. The facility is equipped with both a laser-Doppler anemometer and a laser-induced fluorescence concentration measuring device. The fluorescence induced in a dissolved dye is focused onto an array of photodiodes to enable instantaneous measurement of dye concentration in a column of fluid approximately 0.1 mm in diameter and 5 mm long. Matching of the refractive index in the otherwise inhomogeneous fluid prevents any distortion of the illumination field from this source.

The results obtained with this experimental apparatus have provided the data to substantiate a mixing theory first proposed by Phillips in 1977. In this theory internal waves in the density-stratified fluid are limited in their spectral density by sporadic local instabilities and a breakdown to turbulence. Mixing therefore occurs in intermittent bursts and the local gradient Richardson number remains constant. The thickness of an interfacial layer in the stratified fluids decreases with an overall Richardson number defined in terms of an integral length scale, buoyancy discontinuity and turbulence intensity. Ultimately the interfacial layer becomes limited by diffusive effects.

In ongoing experiments the effect of the conjugation of internal flows on the mixing is being studied. In such flows two stable flow situations are possible, corresponding to the internal Froude number being greater or less than one. Jumps are possible between certain conjugate flow states and the mixing that occurs within such highly turbulent flow zones is being studied.

The results will be applied to mixing across atmospheric temperature inversions and the pycnocline in reservoirs and the ocean.

Publications:

Hannoun, I. A., Fernando, H. J. S., List, E. J., "Turbulence Structure Near a Sharp Density Interface," *J. Fluid Mech.*, 189, 189-209, 1988.

Hannoun, I. A., List, E. J., "Turbulent Mixing at a Shear Free Density Interface," *J. Fluid Mech.*, 189, 211-234, 1988.

Rasi, M., List, E.J., Sullivan, G., Dugan, R., "Mixing in Density-Stratified Conjugate Flows", Proc. 10th Austrulasian Conf. on Fluid Mech., Univ. of Melbourne, Australia, Dec. 1989.

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**Graduate Student, Aeronautics

***Arizona State University

TURBULENT KINETIC ENERGY DISSIPATION IN PLUMES

Investigators: Dimitris Papantoniou,* Regina Dugan,** E. John List

Support: National Science Foundation

The flow structure and entrainment mechanism in the far field of a round vertical buoyant jet have been studied experimentally by use of an optical technique based on laser-induced fluorescence (LIF). A large number of essentially instantaneous tracer concentration profiles were recorded for each experimental run by combining LIF with linear photodiode array imaging and high speed digital data acquisition. Analysis of the resulting high resolution flow images indicates that the far field region is dominated by the periodic passage of structures spanning the entire radial flow extent. Ambient fluid is entrained by vortical motions and is transported to regions deep into the flow interior. The passage frequency of the structures scales with the local mean velocity and flow width. Conditional averaging of the data indicates that in the (downstream) front regions of the structure fluid is rather well mixed and at a higher concentration level than the back and side regions where ambient fluid is intermittently present. This results in an axial concentration gradient within the structure, analogous to the ramplike pattern previously observed in heated air jets. In comparison to the momentum driven flow the ambient fluid presence in the flow interior is greatly increased when body forces are the driving mechanism. The PDF of concentration in the buoyancy-driven plume exhibits about twice the spread compared to the momentum-driven jet, resulting in a twofold increase in the concentration variance. The transition from buoyancy-generated turbulence to ambient turbulence is under investigation.

Publication:

Papantoniou, D., List, E. J., "Large Scale Structure in the Far Field of Buoyant Jets," *J. Fluid Mech.*, 200, 151-190, 1989.

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**Graduate Student, Mechanical Engineering

BREAKING WAVES: THEIR KINEMATIC PROPERTIES AND THEIR INTERACTION WITH THE BOTTOM

Investigators: Catherine Petroff,* Fredric Raichlen

Support: National Science Foundation

This research investigates the kinematic properties of breaking waves and the interaction of these waves with the bottom before, at, and just after breaking. Of particular interest is the region as the broken waves propagate toward shore. During the breaking process velocities are generated which can penetrate to the bottom entraining sediment. If there are bottom-sited structures in the breaking region serious erosion and undermining of the structures may take place. The objective of this research is to gain an understanding of these velocities and their effects on the bottom and on bottom pavements designed to protect against scour.

The early portion of this investigation dealt with the measurement of water particle velocities under plunging and spilling breaking solitary waves. Solitary waves were generated in a wave tank 40 m long, 1.1 m wide, and 0.6 m deep, constructed with glass sidewalls throughout which could be tilted from horizontal to a maximum slope of 2%. A hydraulically driven bulkhead wave generator was mounted at one end of the tank which could be programmed to generate a wide range of waves resulting in spilling and plunging breakers. The investigation used a special laser-Doppler velocimeter (LDV) which was designed to measure water particle velocities close to the bottom and close to the water surface. Some of these results have been reported by Skjelbreia (1987). Papanicolaou and Raichlen (1987) and Papanicolaou and Raichlen (1988) investigated other aspects of the breaking of solitary and cnoidal waves including an estimate of the bubble entrainment by these waves at breaking and the acoustical signal of plunging and spilling breaking waves. Both of these characteristics of breaking waves provide useful descriptions of the differences between these two types of breaking waves.

The current investigation deals with the interaction of these waves with bottom pavement armor; such material would be used to protect a structure founded on a sand bottom from damage due to bottom erosion. First investigating this problem in a fundamental way, the forces caused by solitary and cnoidal waves on spheres located both near the bottom and away from the boundary have been measured. For an isolated sphere it was found that the effect of the boundary on the drag and inertial coefficients was important. The effect of the sheltering of one or more spheres on the forces acting on another sphere was studied also. The sphere arrangements varied from two spheres in line to one sphere surrounded by six others. The effect of sheltering on the forces on one sphere was found to be important only when the clearance between spheres was relatively small. Velocities have been measured, using the LDV, to investigate additional aspects of this behavior. The

results of this portion of the study will be useful in the current phase of the investigation which deals with natural rock pavements. The forces caused by plunging and spilling breaking solitary and periodic long waves on sections of the bottom composed of rock and the associated near bottom velocities are being investigated. The objective of this part of the research is to define the important parameters which influence the effective design of rock blankets for the protection of structures against scour.

Publications:

Skjelbreia, J. C., "Observations of Breaking Waves on Sloping Bottoms by Use of Laser Doppler Velocimetry," W. M. Keck Laboratory Report KH-R-48, 176 pp., May 1987.

Papanicolaou, P., Raichlen, F., "Wave Characteristics in the Surf Zone," Proc. Coastal Hydrodynamics Conf., University of Delaware, 1987.

Raichlen, F., Papanicolaou, P., "Some Characteristics of Breaking Waves," Proc. 21st Inter. Conf. on Coastal Engineering, 1988.

*Graduate Student, Civil Engineering

A STUDY OF TSUNAMIS: THEIR GENERATION, PROPAGATION, AND COASTAL EFFECTS

Investigators: Jerald Ramsden,* Jeffrey Zelt,* Fredric Raichlen

Support: National Science Foundation

An understanding of the generation, propagation, and coastal effects of tsunamis (seismically generated sea waves) is important in mitigating the effects of such waves on coastal-sited structures. Two different investigations are underway which deal with nearshore effects of tsunamis.

Of importance in studying the effect of long waves such as tsunamis on harbors or bays is their interaction with the boundaries. In this connection research has continued studying the process of runup on beaches of constant slope and variable slope caused by solitary waves. These waves were generated in a wave tank 37.3 m long, 0.4 m wide, and 0.6 m deep using a programmable, hydraulically actuated bulkhead wave generator. The profile of the runup on the beach was measured using a video camera with a high speed shutter. To facilitate this, a unique lighting technique was employed where, through the addition of a small amount of milk to the water combined with underwater lighting, it was possible to light only the water keeping the background dark. The resulting video permitted relatively easy data reduction procedures to be used with a precision video editing system. The experimental results of the shape of the runup tongue for a simple plane beach have been compared to a theory based on the numerical solution of a set of long wave equations in the Lagrangian description. The theory compares well to these experimental results and those of previous investigators. Initial experiments also were conducted using a beach with a gradual transition to a horizontal surface which was located at the elevation of the still water level. Thus, as waves ran up the beach and broke the bore which formed propagated shoreward producing the type of inundation one would expect from the shoreward propagation of a tsunami. This aspect of inland flooding is currently being studied.

In another investigation also related to the coastal effects of tsunamis, forces and pressures are being measured on a vertical wall due to an impinging bore. Experiments are conducted in a tilting wave tank 40 m long, 1.1 m wide, and 0.6 m deep which has glass sidewalls throughout with a programmable hydraulically actuated wave generator. By generating a single solitary wave in the tilted tank the position of wave breaking can be controlled thereby generating a bore which propagates shoreward eventually striking the vertical wall. A system of force cells measures the force-time history caused by the bore with flush mounted pressure transducers measuring pressures. High speed motion pictures are taken to define the profile of the bore and the shape of the splash-up on the vertical wall. The latter are

compared simultaneously to the force and pressure measurements. Due to the large vertical accelerations associated with the splash-up it was found that the maximum force occurred after the maximum splash-up was reached. Both experimental and theoretical efforts are continuing on this problem.

Publications:

Zelt, J. A., Raichlen, F., "A Langrangian Model for Wave Induced Harbour Oscillations," Journal of Fluid Mech., in press, 1990.

Ramsden, J. D., Raichlen, F., "Forces on a Vertical Wall Caused by Incident Bores," Journal of the Waterways, Ports, Coastal and Ocean Engr., ASCE, submitted for publication, 1990.

*Graduate Student, Civil Engineering

WAVE AND CURRENT INTERACTIONS WITH A BOTTOM TRENCH

Investigators: Francis Ting,* Fredric Raichlen

Support: Office of Naval Research

This study, completed during this reporting interval, investigated certain aspects of the maintenance dredging of navigation channels in harbors and estuaries. A class of harbors where dredging maintenance is a problem is where the bottom is composed of fine material, i.e., harbors with "muddy bottoms". The bottom material in a dredged navigation trench can be entrained by ships, waves, and currents; thus, the suspended material can create a density stratification in the trench with the trench filled with fluids of two different densities. When the trench is exposed to long waves this creates the possibility of developing internal resonant oscillations in the trench which could accelerate the deterioration of the dredged trench and transport material from the trench into the harbor. It was this problem, i.e., the wave induced motions in a stratified trench, which was investigated both experimentally and theoretically.

The experiments were conducted in a wave tank 37.3 m long, 0.4 m wide, and 0.61 m deep with glass walls throughout and a programmable wave generator driven by a hydraulic system located at one end. The trench was installed in the tank using a false bottom extending from the wave generator to the trench location. A vertical wall extending the full depth in the wave tank provided the necessary downstream boundary for the trench. Since very long surface waves were required to excite the internal waves at a resonant mode of oscillation, the waves in the tank and in the trench were standing waves. A unique device was developed to measure the interfacial wave amplitudes using a scanning laser with a dyed lower dense layer in the trench. A theoretical model was developed which was found to agree well with the results of the experiments. The theory developed was extended to treat the problem of interest: the case of a stratified trench in a fluid of infinite extent where the waves which force the oscillation in the trench are propagating waves.

Publications:

Ting, F. C. K., Raichlen, F., "Wave Interaction with Rectangular Trench in Density-Stratified Fluid," *Jour. Waterway, Port, Coastal, and Ocean Engr.*, ASCE, Vol. 114, No. 5, Sept. 1988.

Ting, F. C. K., "Interaction of Water Waves with a Density-Stratified Fluid in a Rectangular Trench," W. M. Keck Laboratory Report KH-R-50, 305 pp., May 1989.

*Graduate Student, Civil Engineering

MODAL ANALYSIS OF SOLITARY WAVES FORCIBLY GENERATED

Investigators: Theodore Y. Wu

Support: Office of Naval Research, National Science Foundation

The theory of forced nonlinear waves has emerged as a new subject of cardinal importance in mathematical sciences and mechanics. The theory has broad applications to all soliton-bearing systems, including free-surface waves, vortex dynamics, oceanography, meteorology, nonlinear optics and acoustics, superconductors, modern physics, biology, astronomy and other disciplines. Our primary interest is in the disciplines of applied mathematics and fluid mechanics. This subject is relevant to mathematical modelling and development of analytical and numerical methods applicable not only to gravity waves in shallow waters, but also to long waves on a shallow thermocline and wave envelopes in deep water. The chief goal of this study is to secure better understanding of the basic mechanism underlying these phenomena.

The basic mechanism underlying the phenomenon whereby a forcing distribution moving uniformly with a constant transcritical velocity in shallow water can generate, continuously and periodically, a succession of solitary waves, advancing in procession ahead of the disturbance, while a train of weakly dispersive waves develop behind the steadily progressing disturbance is being investigated. This remarkable phenomenon shows that the response of a dynamical system to steady forcing need not asymptotically tend to a steady state, but instead the response can be conspicuously periodic when the system is being forced at resonance.

A family of forced steady solitary waves, all of a permanent form and finite amplitude have been found to exist according to the forced KdV model. Once established these waves will remain permanent in form. The existence of these solutions is significant in that it broadens the class of solitary waves and may have application to understanding the occurrence of certain types of forcing disturbances that yield only local effects, including oceanographic applications to tidal currents over topographies and meteorological observations of mountain lee waves. They may also form a basis for the validation of approximate schemes based on the Boussinesq - KdV class of theories, and provide a primary state of finite amplitude for perturbation and stability studies.

Based on the forced KdV model a Galerkin modal expansion analysis was first developed in this project to investigate the nonlinear stability of a forced steady solitary wave generated by a disturbance steadily moving at the critical speed. The leading two-term analysis can already determine the imaginary part of the eigenvalue quite accurately (with error < 2%), but it requires no less than 400 terms to compute the much smaller real part of the eigenvalue (smaller by 2 to 5 orders than the

imaginary part) on linear theory with a reasonable accuracy. This rather unusual property of the eigenvalue (namely, with a large ratio of the imaginary to real part) has been found to be quite general for the stability of forced nonlinear waves in a subsequent study reported below.

Publications:

Wu, T. Y., Invited Address: "Forced Generation of Solitary Waves," In: Applied Mathematics, Fluid Mechanics, Astrophysics: A Symp. to honor C. C. Lin (eds. D. J. Benney, F. H. Shu and C. Yuan), pp. 198-212, World Scientific, 1988.

Wu, T. Y., "Generation of Upstream-advancing Solitons by Moving Disturbances," J. Fluid Mech., 184, 75-99, 1987.

NONLINEAR STABILITY OF THE SOLITARY WAVES FORCIBLY GENERATED

Investigators: Roberto A. Camassa*, Theodore Y. Wu

Support: National Science Foundation, Office of Naval Research

The theory of hydrodynamic nonlinear stability is being rapidly developed in the recent two decades, but for the general case concerning stability of nonlinear waves being forced at resonance, the theory is in its infancy. The goal of this project is to examine the underlying eigenvalue problem, its spectral properties, the principle of exchange of stabilities, multi-stationary states, bifurcation patterns, and new physical mechanisms of solution growth. Our new research results have shown that the instability of nonlinear waves under forcing at resonance has salient features drastically different from those in the classical cases.

Linear and nonlinear stability analysis has been carried out for a steady solitary wave forcibly generated by steadily moving disturbances at transcritical speeds. Singular perturbation methods are used to obtain local spectral analysis of the fixed-point solutions, and are complemented by numerical analysis, with very high accuracy, of the global spectral properties of the characteristic perturbation solutions. The results show that in the evolutionary transcritical range, the eigenvalues have only four branches, $\sigma = \pm \sigma_r \pm iw$, where σ_r and w are real and $i = \sqrt{(-1)}$, with $\sigma_r \ll w$. The remarkable feature of the ratio σ_r/w being small therefore infers that waves evolve under forcing with a slow growth, at the rate of σ_r .

In the bifurcating supercritical regime characterizing steeper forced waves moving with moderate supercritical Froude number, the eigenvalue σ is purely real, which implies wave growth and possible soliton emission. In this parametric regime, a new finding of great interest is the existence of another stationary solution which is weaker than Wu's forced wave solution and is found to be stable, so that given sufficient time, the stronger wave solution always bifurcates towards the weaker one. In the hypercritical regime beyond the bifurcating range, the eigenvalue spectrum becomes continuous, and the perturbed motion is asymptotically all local, with no local evolution.

Publications:

Camassa, R. and Wu, T. Y., "Stability of Forced Steady Solitary Waves," accepted for publication, Phil. Trans. Roy. Soc. A., London, 1990.

Camassa, R. A., "Multiple Stationary Solutions for the Forced KdV Equation," In: Engineering Science, Fluid Dynamics: A Symposium to honor T. Y. Wu, (ed. G. T. Yates), pp. 45-58, World Scientific, 1990.

Camassa, R. A., "Part I: Forced Generation and Stability of Nonlinear Waves," Ph.D. thesis, California Institute of Technology, 1990.

Camassa, R. A. and Wu, T. Y., "Stability of Some Stationary Solutions for the Forced KdV Equation," submitted to Physica D. Proceedings for CNLS Conference, "Nonlinear Science, The Next Decade", May 21-25, 1990, Los Alamos, NM.

*President's Postdoctoral Fellow, Los Alamos National Laboratory. (Ph.D. graduate in Engineering Science)

THE KdV MODEL WITH BOUNDARY FORCING

Investigators: Robert A. Camassa*, Theodore Y. Wu

Support: Office of Naval Research, National Science Foundation

The problem of solitons and nonlinear waves generated by boundary forcing imposed on the KdV model, previously studied numerically in the literature, has been analyzed by applying, for the first time, the inverse scattering transform (IST) scheme (originally devised for unbounded space) to the $1/4$ -plane ($\chi \geq 0$ in space, $\tau \geq 0$ in time) problem, with some simplifying assumptions. This analytical method is found capable of providing quantitative predictions of such main variables as the total number of solitons generated by a specific boundary forcing, their amplitudes and phases, etc. These predictions are found in broad agreement with numerical results.

Publication:

Camassa, R.A., Wu, T. Y., "The Korteweg-DeVries Model with Boundary Forcing," Wave Motion 11, 495-506, 1989.

*President's Postdoctoral Fellow, Los Alamos National Laboratory. (Ph.D. graduate in Engineering Science)

ANTI-SYMMETRIC SOLUTIONS OF THE FORCED KdV EQUATION

Investigators: George T. Yates, Theodore Y. Wu

Support: Office of Naval Research, National Science Foundation

An anti-symmetric family of steady solutions to the forced KdV equation has been identified which decay exponentially at infinity and can move at arbitrary transcritical speed when accompanied by proper forcing distributions. The linear and nonlinear stability of these steady state solutions are investigated over a wide range of speeds and wave amplitudes. Unlike the symmetric family of steady solutions for the fKdV equation (as reported in the foregoing), no analytical method is available for evaluating local stability of the solution because of an irregular singularity of the basic equation that render the fixed-point solutions unattainable in closed analytical form. In spite of this deficiency, regions of stability have been investigated and compared to results from the numerical integration of the forced KdV model. The appearance of unstable modes with periodic oscillations are found by linear theory and are observed numerically using the nonlinear model.

Publication:

Yates, G. T., "Some Antisymmetric Solutions with Permanent Form of the Forced KdV Equation," In: Engineering Science. Fluid Dynamics: A Symposium to honor T. Y. Wu, (ed. G. T. Yates), pp. 119-131, World Scientific, 1990.

SCATTERING AND DIFFRACTION OF SOLITARY WAVES BY A VERTICAL CYLINDER

Investigators: Keh Han Wang*, Theodore Y. Wu, George T. Yates

Support: Office of Naval Research, National Science Foundation

This numerical and experimental study establishes the generalized Boussinesq equations as a useful theoretical model for a new class of problems in naval hydrodynamics involving scattering and diffraction of nonlinear and dispersive waves by structures and vehicles. The three-dimensional wave patterns throughout the wave impact on a vertical circular cylinder and the time-varying wave impact force have several salient features of interest. The scattered waves are radiated outward with a nearly cylindrical symmetry centered at the cylinder. The forward scattered primary wave is found to recover its uniform phase (i.e., with the wave crest keeping straight abreast) after leaving the cylinder, while the uneven wave amplitude along the crest develops into a transverse wave motion. The wave impact force has a positive first half and a weaker negative trailing half, and thus appears in variance with Morison's formula, especially for larger amplitude waves. Numerical results further reveal the relative importance of linear, nonlinear and dispersive effects before, during, and after the wave impact. Another conspicuous feature of the solution is that during the swift and transient wave-body encounter, both the nonlinear and dispersive effects are found to vary rapidly in magnitude and phase relative to the linear terms of the governing equations. Preliminary experimental results show good agreement with the numerical model.

Publication:

Wang, K. H., Wu, T. Y., Yates, G. T., "Scattering and Diffraction of Solitary Waves by a Vertical Cylinder," In: Proc. of 17th Symp. on Naval Hydrodynamics, pp. 513-522, 1989.

*University of Houston, Houston, Texas

THEORETICAL AND EXPERIMENTAL STUDIES OF THE FORCED GENERATION OF PRECURSOR SOLITONS

Investigators: S. J. Lee*, Theodore Y. Wu, George T. Yates

Support: Office of Naval Research, National Science Foundation

This work presents the first known experimental validation of the principal theoretical models employed for predicting forced generation and emission of precursor solitons by transcritical disturbances. A broad agreement between experiments and both the generalized Boussinesq model and the fKdV equation was found for the depth Froude number ($F = U/\sqrt{gh}$; U being the constant velocity of the disturbance, g the gravity acceleration, and h the undisturbed water depth) lying within a narrow near-critical range of $0.9 < F < 1.1$. Just outside this range, wave breaking was found to occur; this real-fluid phenomenon appear to be of fundamental importance and deserves further research efforts.

Publications:

Lee, S. J., Yates, G. T., Wu, T. Y., "A Theoretical and Experimental Study of Precursor Solitary Waves Generated by Moving Disturbances," In: Nonlinear Water Waves (eds. K. Horikawa, H. Maruo), pp. 365-372, Springer-Verlag, Berlin, 1988.

Lee, S. J., Yates, G. T., Wu, T. Y., "Experiments and Analyses of Upstream-advancing Solitary Waves Generated by Moving Disturbances," J. Fluid Mech., 199, 569-593, 1989.

*Chungnam National University, Daeduk Science Town, Korea (Ph.D. graduate in Engineering Science)

GENERATION AND PROPAGATION OF INTERNAL SOLITARY WAVES

Investigators: J. L. Zhu*, Theodore Y. Wu, George T. Yates

Support: Office of Naval Research, National Science Foundation

Motivated by the observation of internal solitary waves moving within the pycnocline of the oceans, we have investigated the generation of internal waves by moving disturbances. Within a range of transcritical speeds (relevant to the internal wave modes), periodic generation of internal solitary waves have been observed both experimentally and numerically, with salient features closely resembling those for the case of a single layer of homogeneous fluid. Both a forced KdV model, and a generalized Boussinesq model have been developed, each having respective advantages and restrictions on their application. The detailed density profile is found to be important in making accurate predictions of internal wave generation periods.

Publications:

Zhu, J. L., Wu, T. Y., Yates, G. T., "Internal Solitary Waves Generated by Moving Disturbances," In: Stratified Flows (eds. E. J. List, G. H. Jirka), ASCE (3rd Int. Symp. of Density Stratified Flows, Pasadena, CA, USA, Feb. 3-5, 1990)

Zhu, J. L., Wu, T. Y., Yates, G. T., "Upstream Internal Solitons Generated by Moving Disturbances," Int. Conf. on Fluid Mech., Beijing, China, pp. 517-522, July 1-4, 1987.

*Dept. Engineering Mechanics, Tsinghua University, Beijing, China (Ph.D. graduate in Engineering Science)

PRECURSOR SOLITONS GENERATED BY THE THREE-DIMENSIONAL DISTURBANCES MOVING IN A CHANNEL

Investigators: D. M. Wu*, Theodore Y. Wu

Support: Office of Naval Research, National Science Foundation

The two-dimensional long wave formulation has been extended to include three-dimensional disturbances in an effort to model ships moving with transcritical speeds on shallow water in laterally confined waters. For surface pressure type forcings, numerical solutions were obtained to predict the upstream-advancing solitary waves generated by three-dimensional transcritical disturbances moving in a channel; the precursor solitons are invariably two-dimensional and stretched straight across the channel. The trailing wave pattern is conspicuously three dimensional. From detailed studies of the numerical results, an important correspondence rule has been derived which correlates three-dimensional forcing functions with equivalent two-dimensional ones. This rule will be useful in applications to complicated three-dimensional problems.

Publication:

Wu, D. M., Wu, T. Y., "Precursor Solitons Generated by Three-dimensional Disturbances Moving in a Channel," In: Nonlinear Water Waves (eds. K. Horikawa, H. Maruo), pp. 69-75, Springer-Verlag, Berlin, 1988.

*Harbin Shipbuilding Engineering Institute, Harbin, China

GENERATION AND PROPAGATION OF NONLINEAR WATER WAVES IN A CHANNEL WITH VARIABLE CROSS SECTION

Investigators: Michelle H. Teng*, Theodore Y. Wu

Support: Office of Naval Research, National Science Foundation

The generalized Boussinesq type equations and the forced KdV equation are derived for weakly nonlinear and weakly dispersive water waves in a channel with arbitrary cross section whose shape and dimensions may vary in space and time. Analytical solutions for three specific configurations, namely, rectangular, triangular and semi-circular cross sections are obtained in closed form. These new models may also include moving bodies, floating or submerged, as external forcings which can produce upstream advancing solitons which may then propagate with modulated amplitude, velocity and phase. The effective strength of forcing is directly related to the blockage ratio and the specific shape of the cross section is found to affect the dispersive terms in the equations of motion.

Publications:

Teng, M. H., Wu, T. Y., "Generation and Propagation of Nonlinear Water Waves in a Channel with Variable Cross Section," In: Engineering Science. Fluid Dynamics: A Symposium to honor T. Y. Wu (ed. G. T. Yates), pp. 87-108, World Scientific, 1990.

Teng, M. H., "Forced Emissions of Nonlinear Water Waves in Channels of Arbitrary Shape," Ph.D. thesis, California Institute of Technology, 1990

Graduate Student, Engineering Science

STANDING WAVE SOLUTIONS OF THE GENERALIZED BOUSSINESQ MODEL

Investigators: Gary S. Guthart*, Theodore Y. Wu

Support: Office of Naval Research, National Science Foundation

Theoretical, numerical and experimental efforts have been devoted to investigate the phenomenon of forced, nonlinear, standing waves on shallow water contained in a rectangular channel which undergoes vertical oscillations. The generalized Boussinesq equations are solved using a pseudo-spectral scheme which allows wave propagation in two horizontal directions and admits arbitrary bottom topography. With vertical forcing at a frequency near one half the natural frequency of the tank width, a stable "standing solitary wave" develops and sloshes across the width of the tank. For moderate amplitudes of the forcing, the resulting wave amplitude can be several times the water depth. Comparisons between experiments and numerical results are consistent.

Recently, a multiple scales technique has been used to investigate forced and free waves. In both cases, a modulated hyperbolic tangent wave envelope along the tank length has been identified. Preliminary laboratory observations show good agreement between theory, computations and experiments.

This is a preliminary report of work in progress, and as yet no written reports are available for distribution.

*Graduate student in Engineering Science

D. AIR QUALITY, ATMOSPHERIC CHEMISTRY AND AEROSOL PHYSICS

PROTECTION OF WORKS OF ART FROM DAMAGE DUE TO AIRBORNE PARTICULATE MATTER

Investigators: William W. Nazaroff*, Mary Ligocki, Theresa Fall,
Lynn Salmon, Mike Jones**, Harvey Liu**, Timothy Ma**,
Glen R. Cass

Support: J. Paul Getty Conservation Institute

The soiling of works of art due to deposition of airborne particulate matter poses a major hazard to museum collections. Over long periods of time, dark deposits build up on the surfaces of paintings, sculpture and stone buildings, necessitating cleaning procedures that are both expensive and that pose some risk to the works themselves.

A study is underway designed to understand how to control or prevent this particle deposition problem. Airborne particle concentrations, size distributions and chemical composition measurements have been made inside and outside of five museums in the Los Angeles area. The flux of particles to interior surfaces also has been measured. These field experimental data are being used to test theoretical computer-based models that account for the size distribution and chemical composition of the indoor aerosol and the particle flux to surfaces. The completed indoor air quality model is being used to evaluate alternative procedures for controlling the particle deposition process.

Publications:

Ligocki, M. P., Liu, H. I., Cass, G. R., John, W., "Measurements of Particle Deposition Rates Inside Southern California Museums," Aerosol Science and Technology, in press, 1990.

Nazaroff, W. W., Ligocki, M. P., Ma, T., Cass, G. R., "Particle Deposition in Museums: Comparison of Modeling and Measurement Results," Aerosol Science and Technology, in press, 1990.

Nazaroff, W. W., Cass, G. R., "Mathematical Modeling of Indoor Aerosol Dynamics," Environmental Science and Technology, 23, 157-166, 1989.

Nazaroff, W. W., Cass, G. R., "Mass-Transport Aspects of Pollutant Removal at Indoor Surfaces," Environment International, 15, 567-584.

Ligocki, M. P., Salmon, L. G., Fall, T., Jones, M. C., Nazaroff, W. W., Cass, G. R., "Characteristics of Airborne Particles Inside Southern California Museums," submitted to Atmospheric Environment, 1990.

Nazaroff, W. W., Cass, G. R., "Protecting Museum Collections from Soiling Due to the Deposition of Airborne Particles," submitted to Atmospheric Environment, 1990.

Nazaroff, W. W., Cass, G. R., "Particle Deposition from a Natural Convection Flow Onto a Vertical Isothermal Flat Plate." Journal of Aerosol Science, 18, 445-455, 1987.

Nazaroff, W. W., "Mathematical Modeling and Control of Pollutant Dynamics in Indoor Air," Ph.D. Thesis, California Institute of Technology, 1989.

*Graduate Student, Environmental Engineering Science

**Undergraduate Student

PROTECTION OF WORKS OF ART FROM DAMAGE DUE TO PHOTOCHEMICAL SMOG

Investigators: Paul M. Whitmore, William W. Nazaroff*, C. Pam DeMoor**, Cynthia Wittman**, Kaitlin Drisko**, James R. Druzik***, Daniel Grosjean****, Glen R. Cass

Support: J. Paul Getty Conservation Institute

The fading of pigments is a major hazard to works of art. Work in our laboratories has shown that a number of widely-used artists' pigments are not ozone-fast, and will fade during a 95-day exposure to 0.40 ppm ozone in the absence of light. The extent of this ozone hazard to works of art has been assessed through examination of more than 150 organic pigment samples obtained from the Fogg Museum at Harvard. The chemistry of the attack of ozone on artists' pigments has been investigated via GC/MS analysis of the pigments and their reaction products.

The distribution of ozone and NO₂ concentrations in the indoor atmosphere of museums in Southern California has been assessed via a series of field experiments. Mathematical models for the behavior of pollutants inside museums and archives have been developed and tested. Strategies for protecting works of art from damage due to air pollutants are being developed, including selection of pollutant-resistant pigments, pollutant removal via ventilation system redesign, encapsulation of works of art, and the use of protective binders and coatings.

Publications

Grosjean, D., Whitmore, P. M., Cass, G. R., "Ozone Fading of Triphenylmethane Colorants: Reaction Products and Mechanisms," Environmental Science and Technology, 23, 1164-67, 1989.

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Cass, G. R., Druzik, J. R., Grosjean, D., Nazaroff, W. W., Whitmore, P. M., Wittman, C. L., "Protection of Works of Art from Photochemical Smog," Environmental Quality Laboratory Report No. 28, California Institute of Technology, Pasadena, CA, 1988.

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**Undergraduate Student

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****Visiting Associate, Division of Chemistry and Chemical Engineering

ACQUISITION OF ACID VAPOR AND AEROSOL CONCENTRATION DATA IN THE SOUTH COAST AIR BASIN

Investigators: Paul Solomon, Theresa Fall, Lynn Salmon, Susan Larson*, Philip Lin**, Harvey Liu**, Mike Jones**, Frank Vasquez**, David Cole**, Sandra Blumhorst**, Nancy Drehwing**, Doug Gray**, Betsy Andrews**, Glen R. Cass

Support: State of California Air Resources Board, South Coast Air Quality Management District

A field experiment has been conducted to measure the spatial and temporal concentration distribution of gas phase acids (HNO_3 , HCl , HBr , HF , formic acid) and related particulate phase species in the Southern California atmosphere. Atmospheric nitric acid concentrations were found to peak in the summer months, with maximum 24-hour average concentrations in the vicinity of 10 ppb. Conversion of nitric acid to aerosol phase nitrates was found to be a dominant factor in the production of high airborne particle concentrations in the eastern portion of the Los Angeles basin. Peak 24-hour average PM10 concentrations (particulate matter in sizes below 10 μm aerodynamic diameter) reached $299 \mu\text{gm}^{-3}$ in the Riverside area during October 1986, a factor of 2 higher than the Federal PM10 air quality standard, and 6 times higher than allowed by California air quality standards. More than $100 \mu\text{gm}^{-3}$ of that peak aerosol burden consisted of aerosol nitrate plus associated ammonium ion. Data collected during this experiment have been used to devise the governmental air pollution abatement plans for PM10 in the Los Angeles area.

Publications:

Solomon, P. A., Fall, T., Salmon, L., Cass, G. R., Gray, H. A., Davidson, A., "Chemical Characteristics of PM10 Aerosols Collected in the Los Angeles Area," JAPCA, 39, 154-163, 1989.

Pierson, W. R., Brachaczek, W. W., Japar, S. M., Cass, G. R., Solomon, P. A., "Dry Deposition and Dew Chemistry in Claremont, California During the 1985 Nitrogen Species Methods Comparison Study," Atmospheric Environment, 22, 1657-1664, 1988.

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Solomon, P. A., Fall, T., Salmon, L. G., Lin, P., Vasquez, F., Cass, G. R., "Acquisition of Acid Vapor and Aerosol Concentration Data for Use in Dry Deposition Studies in the South Coast Air Basin," Environmental Quality Laboratory Report No. 25, California Institute of Technology, Pasadena, CA, 1988.

*Graduate Student, Environmental Engineering Science

**Undergraduate Student, Caltech

CONTROL OF THE DRY DEPOSITION OF NITROGEN-CONTAINING AIR POLLUTANTS

Investigators: Armistead G. Russell*, Kenneth F. McCue, Glen R. Cass

Support: State of California Air Resources Board

An improved mathematical model for computing the dry deposition flux of nitrogen-containing air pollutants is being developed. The model will be used to study the effect of candidate emission control strategies on acid dry deposition in Southern California.

This is a preliminary report of work in progress, and as yet no written reports are available for distribution.

*Assistant Professor, Mechanical Engineering Department, Carnegie-Mellon University

STUDIES OF VISIBILITY-REDUCING ORGANIC AEROSOLS IN THE
DESERT SOUTHWESTERN UNITED STATES (SCENES-ORIGIN OF
ORGANICS STUDY)

Investigators: Monica Mazurek, Bernd R. T. Simoneit*, Glen R. Cass

Support: The Electric Power Research Institute, AeroVironment, Inc.

Organic particulate matter is a major contributor to the visibility-reducing aerosol present in the vicinity of the national parks in the desert southwestern United States. Identification of the emission sources that contribute to this organic aerosol is being pursued. High resolution gas chromatography and gas chromatography/mass spectrometry analyses of aerosol samples taken by the SCENES air monitoring network are being undertaken to search for organic molecules that act as tracers for particulate emission source types. It has been found that wood smoke and plant waxes are two of the significant contributors to the organic aerosol samples studied.

Publications:

Mazurek, M. A., Cass, G. R., Simoneit, B. R. T., "Quantification of the Source Contributions to Organic Aerosols in the Remote Desert Atmosphere," Environmental Quality Laboratory Report prepared for the Electric Power Research Institute, California Institute of Technology, Pasadena, CA, 1988.

*Professor, Organic Geochemistry Group, College of Oceanography, Oregon State University

DEVELOPMENT OF STRATEGIES FOR VISIBILITY IMPROVEMENT USING AN IMAGE PROCESSING-BASED VISIBILITY MODEL

Investigators:

Susan Larson*, Kenneth McCue, Mary Ligocki,
H. Andrew Grey, Kevin J. Hussey**, Frederick Luce**,
Jeff Hall**, Glen R. Cass

Support:

State of California Air Resources Board, William and Flora Hewlett Foundation, Gifts to the Environmental Quality Laboratory, National Aeronautics and Space Administration

Light scattering calculations based on pollutant properties measured during intense pollution episodes can be used to add haze to the foreground of clear sky pictures by image processing techniques. The ability of these light scattering and absorption calculations to accurately reproduce the visual effects that occur during smog episodes is being verified by comparing the synthetic smog images to digitized photos of actual high pollution events. The completed visibility model is being used as part of a systematic investigation of emission control strategies which could be used to achieve a deliberate improvement in summer midday low-visibility conditions in the Los Angeles area.

Publications:

Larson, S. M., Cass, G. R., "Characteristics of Summer Midday Low Visibility Events in the Los Angeles Area," Environmental Science and Technology, 23, 281-289, 1989.

Larson, S. M., Gray, H. A., Cass, G. R., "Atmospheric Carbon Particles and the Los Angeles Visibility Problem," Aerosol Science and Technology, 10, 118-130, 1989.

Larson, S. M., Cass, G. R., Hussey, K. J. and Luce, F., "Verification of Image Processing-Based Visibility Models," Environmental Science and Technology, v. 22, pp. 629-637, 1988.

Larson, S. M., "A Study of Summer Midday Low-Visibility Events in the Los Angeles Area," Ph.D. Thesis, California Institute of Technology, 1988.

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**Image Processing Laboratory, Jet Propulsion Laboratory

CHARACTERIZATION OF ORGANIC AEROSOLS IN SOURCE EMISSIONS AND IN AMBIENT AIR

Investigators: Lynn Hildemann*, Monica Mazurek, Gregory R. Markowski, Bernd Simoneit**, Glen R. Cass

Support: U. S. Environmental Protection Agency, William and Flora Hewlett Foundation, Gifts to the Environmental Quality Laboratory

The relationship between the chemical composition of organic compounds in source emissions and the composition of organics observed in atmospheric particulate matter is being investigated. The objectives are to identify the major sources of organic particulate matter, to accurately characterize the kinds of organic aerosols being emitted by various source types, and to investigate the extent to which secondary organic aerosols are produced by chemical reactions in the atmosphere. Particulate emissions from a wide range of major aerosol source types have been collected using a dilution stack sampling system specially constructed to simulate the atmospheric condensation and aging processes normally experienced within a stack plume containing organic air pollutants. Analysis of these samples by high-resolution gas chromatography and gas chromatography/mass spectrometry is being used to define the characteristic organic compound signature for each source type. A method for identifying the relative importance of different emission sources in contributing to the organic aerosol species loading present in the atmosphere will be tested by comparing these source signatures to the chemical composition of ambient particulate matter samples using a fluid mechanically-based atmospheric transport model.

Publications:

Hildemann, L. M., Cass, G. R., Markowski, G. R., "A Dilution Stack Sampler for Collection of Organic Aerosol Emissions: Design, Characterization and Field Tests," Aerosol Science and Technology, 10, 193-204, 1989.

Mazurek, M. A., Cass, G. R., Simoneit, B. R. T., "Interpretation of High-Resolution Gas Chromatography and High-Resolution Gas Chromatography/Mass Spectrometry Data Acquired from Atmospheric Aerosol Samples," Aerosol Science and Technology, 10, 408-420, 1989.

Mazurek, M. A., Simoneit, B. R. T., Gray, H. A., Cass, G. R., "Quantitative High-Resolution Gas Chromatography/Mass Spectrometry Analyses of Carbonaceous Fine Aerosol Particles," International Journal of Environmental Analytical Chemistry, 29, 119-139, 1987.

Hildemann, L. M., "A Study of the Origin of Atmospheric Organic Aerosols," Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1989.

14

*Graduate Student, Environmental Engineering Science

**Professor, Environmental Geochemistry Group, College of Oceanography,
Oregon State University

MODELING OF ATMOSPHERIC POLLUTANT CONCENTRATIONS DURING THE SOUTHERN CALIFORNIA AIR QUALITY STUDY

Investigators: Robert Harley*, Binqiang Shi*, Glen R. Cass,
John H. Seinfeld

Support: Coordinating Research Council

A cooperative research effort has begun between Carnegie-Mellon University and Caltech. The objective is to employ photochemical airshed models as a tool for understanding the relationship between pollutant emissions and air quality observed for gaseous pollutants during the recent Southern California Air Quality Study (SCAQS). The Caltech portion of this research effort involves modeling the emissions-to-air-quality relationships for gas-phase organic pollutants (Prof. Cass and Robert Harley) and the construction of novel model performance tests for O_3 , NO_2 and other important inorganic pollutant species (Prof. Seinfeld and Binqiang Shi).

This is a preliminary report of work in progress, and as yet no written reports are available for distribution.

*Graduate Student, Environmental Engineering Science

DETERMINATION OF ORGANIC COMPOUNDS PRESENT IN AIRBORNE PARTICULATE MATTER

Investigators: Wolfgang Rogge*, Bernd R. T. Simoneit**, Monica Mazurek,
Lynn Hildemann*, Glen R. Cass

Support: South Coast Air Quality Management District

Organic compounds constitute the largest single contributor to the fine particulate matter burden in the Los Angeles atmosphere. Typically 30% of the local fine aerosol mass is carbonaceous. These airborne carbon particles lead to visibility reduction and many of the organics found on aerosols are known carcinogens and mutagens.

A key problem faced by agencies charged with controlling airborne particulate matter is that aerosol carbon is emitted from a very large number of source types that are not easily distinguished from one another once their effluents have mixed in the atmosphere. Carbon particles emitted from charbroiling at restaurants look much like carbon particles emitted from wood smoke at home fireplaces if nothing more than an elemental analysis is performed. Since carbon particle emissions often result from combustion of fuels or other materials that contain little more than carbon and hydrogen, these particles often are not accompanied by co-occurring trace metals in quantities sufficient to permit source identification by receptor modeling techniques. The key to resolving questions about source/receptor relationships for airborne carbon particles is to develop methods that relate observed air quality to sources on the basis of the chemical compounds found in the organic aerosol. In the present project, the organic compounds found in the aerosol in Southern California are being quantified by high resolution GC and GC/MS techniques.

This is a preliminary report of work in progress, and as yet no written reports are available for distribution.

*Graduate Student, Environmental Engineering Science

**Professor, Environmental Oceanography Group, Oregon State University

PROTECTION OF WORKS OF ART FROM DAMAGE DUE TO ATMOSPHERIC NITRIC ACID

Investigators: Lynn Salmon*, Daniel Grosjean**, Glen R. Cass

Support: Getty Conservation Institute

A problem of increasing concern to those responsible for museum collections is the intrusion of air pollutants from the outdoor atmosphere. There is substantial evidence that air pollutants such as ozone (O_3), sulfur dioxide (SO_2), nitrogen dioxide (NO_2) and particulate matter cause significant damage to cultural property. In addition to NO_2 , a variety of nitrogenous air pollutants occur as a mixture in outdoor air, including nitric oxide, aerosol nitrates, nitrous acid and nitric acid. However, very little is known about nitric acid concentrations inside typical facilities where works of art are displayed.

Preliminary tests suggest that nitric acid vapor is capable of inducing rapid fading and color shifts in a variety of important artists' colorants. This study is to determine whether or not nitric acid at the levels found to be drawn into museums from outdoors is capable of causing damage to the colorants used in works of art. The research effort consists of several parts: First, to identify those pigments that are susceptible to HNO_3 damage, chamber studies of the fading and color changes observed in artists' pigments upon exposure to ppb levels of HNO_3 in purified air will be conducted. The chemical mechanisms by which HNO_3 attacks these susceptible colorants will be investigated to confirm that HNO_3 is indeed responsible for the observed color changes. Experimental data on indoor and outdoor HNO_3 levels measured in five Los Angeles area museums will be evaluated to determine the HNO_3 flux to museum collection surfaces over time. Finally, advice will be provided on methods for protecting museum collections from damage due to HNO_3 vapor exposure.

Publication:

Salmon, L. G., Nazaroff, W. W., Ligocki, M. P., Jones, M. C., Cass, G. R., "Nitric Acid Concentrations in Southern California Museums," Environmental Science and Technology. 24:7, 1004-1013, 1990.

*Research Engineer, EQL

**Visiting Associate in Chemical Engineering

VALIDITY OF CURRENT AEROSOL MODELS FOR CALCULATING GAS-AEROSOL EQUILIBRIUM, WATER CONTENT AND SIZE DISTRIBUTIONS, AND RELATIVE CONTRIBUTIONS OF VARIOUS SOURCE TYPES TO VISIBILITY

Investigators: Annmarie Eldering*, Anthony Wexler**, K. C. Moon***,
Chris Pilinis***, Suzanne V. Hering****, Glen R. Cass,
John H. Seinfeld

Support: California Air Resources Board

The South Coast Air Basin of California experiences the highest levels of secondary aerosol in the country. A prime goal of the Southern California Air Quality Study (SCAQS) was to obtain a data base for the development and evaluation of models capable of assessing the effect of primary gaseous and particulate emission changes on ambient aerosol levels, including acid deposition and visibility. Although every individual particle is most likely unique, the Los Angeles aerosol can be characterized generally as a mixture of inorganic species (sulfates, nitrates, ammonium), carbonaceous species (primary and secondary organic and elemental carbon-containing species), soil dust, metals, sea salt, and water. Key needs that must be addressed in developing effective control strategies for particulate matter are: (1) to relate primary gaseous emissions of ROG, NO_x, SO₂, and NH₃ to aerosol composition; (2) to relate primary particulate emissions of carbon, sulfur, sea salt and industrial effluents to aerosol composition; (3) to determine the role of aerosol water in measured PM10 concentrations and to relate water levels to those of other aerosol species; and (4) to determine the relative contributions of various aerosol components and water to atmospheric visibility degradation. These issues are being investigated using the data base accumulated during the SCAQS experiment.

This is a preliminary report of work in progress, and as yet no written reports are available for distribution.

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****Visiting Associate in Chemical Engineering

OPTIMAL STRATEGIES FOR AIR POLLUTION CONTROL

Investigators: Robert Harley*, Glen R. Cass

Support: Gifts to the Environmental Quality Laboratory

Receptor-oriented air quality models are very simple but accurate, and can identify the emission sources contributing to particulate air quality problems based on matching the trace element content of source emissions and atmospheric samples. Pinpointing the combination of pollutant sources responsible for a problem now does not automatically shed much light on how to devise the best emission control strategy to improve air quality. In this research, mathematical programming techniques are being developed that will permit receptor models to be used to identify the least costly combination of control devices needed to solve complex regional particulate air quality problems.

Publication:

Harley, R. A.*, Hunts, S. E., Cass, G. R., "Strategies for the Control of Particulate Air Quality: Least-Cost Solutions Based on Receptor-Oriented Models," Environmental Science and Technology, 23, 1007-1014, 1989.

*Graduate Student, Environmental Engineering Science

CONTROL OF ATMOSPHERIC AEROSOL NITRATE AND NITRIC ACID CONCENTRATIONS

Investigators: Armistead Russell*, Kenneth F. McCue**, Glen R. Cass

Support: State of California Air Resources Board, Gifts to the Environmental Quality Laboratory

A grid-based air quality model has been used to study the effect of specific emission control measures on atmospheric NO_2 , total inorganic nitrate (TN), HNO_3 , aerosol nitrate, PAN, NH_3 , and ozone concentrations in the Los Angeles area. NO_x and reactive hydrocarbon (RHC) emission reductions of up to 61% and 37%, respectively, were examined. NO_2 and TN concentration reductions in excess of 50% averaged over 20 monitoring sites would be achieved at the highest level of emission control studied. The distribution of TN air quality improvements between HNO_3 and aerosol nitrate would be affected by the NH_3 emission rate of the NO_x control technologies employed. Peak one-hour O_3 concentrations at many sites in the eastern portion of the air basin studied would decline by more than 25% at the highest NO_x and RHC control levels studied, with the final increment of NO_x control alone capable of producing O_3 concentration improvements at locations with the highest O_3 concentrations.

Publications:

Russell, A. G., McCue, K. F., Cass, G. R., "Mathematical Modeling of the Formation of Nitrogen-Containing Air Pollutants - 1. Evaluation of an Eulerian Photochemical Model," Environmental Science and Technology, 22, 263-271.

Russell, A. G., McCue, K. F., Cass, G. R., "Mathematical Modeling of the Formation of Nitrogen-Containing Air Pollutants - 2. Evaluation of the Effect of Emission Controls," Environmental Science and Technology, 22, 1336-1346.

*Assistant Professor, Mechanical Engineering Department, Carnegie-Mellon University

**Staff Scientist

FORMATION AND GROWTH OF AEROSOLS IN ATMOSPHERIC PHOTOCHEMISTRY

Investigators: Daniel Grosjean, Sonia Kreidenweis*, Suzanne Paulson**, Jennifer E. Stern*, Shih-chen Wang**, Dale Warren, Fangdong Yin*, John H. Seinfeld, Richard C. Flagan

Support: National Science Foundation, Coordinating Research Council

Gaseous compounds released into the atmosphere from anthropogenic or natural sources undergo photochemical transformations that produce condensable vapors. These vapors then form aerosol by condensation on the surfaces of existing particles or by homogeneous nucleation. Aromatic hydrocarbons are important components of anthropogenic emissions. An experimental study of this system has been performed in an outdoor smog chamber. Aerosol size distributions were measured as a function of time in toluene. *m*-xylene, ethylbenzene and 1,3,5-trimethylbenzene photooxidations were used to determine the rates of new particle formation and the effects of initial particles on aerosol formation and growth. Aerosol yields from the aromatic gas-phase photo-oxidations were found to be 2-5% by mass of the starting aromatic species. Simulations of the aerosol behavior in these experiments have been carried out using an integral model that includes a vapor source, homogeneous nucleation, condensational growth, and particle loss by deposition. Predictions from the model are in relatively good agreement, but indicate that the nucleation mechanism in these systems is still not completely understood. In particular, the physical properties that govern aerosol formation from the condensable reaction products are not well known.

Smog chamber experiments have also been undertaken to study the photochemical oxidation mechanisms and aerosol formation from dimethyl sulfide and dimethyl disulfide. These systems are particularly attractive for the study of aerosol formation since only two condensable species, sulfuric acid and methane sulfonic acid, are produced, and the properties of these species are well known. In parallel with the smog chamber studies, controlled laboratory studies of homogeneous nucleation of a single vapor species and binary nucleation of two vapors are being carried out.

Publications:

Stern, J. E., Flagan, R. C., Grosjean, D., Seinfeld, J. H., "Aerosol Formation and Growth in Atmospheric Aromatic Hydrocarbon Photooxidation," *Env. Sci. & Tech.*, 21, 1224-1231, 1987.

Okuyama, K., Kousaka, Y., Warren, D. R., Flagan, R. C., Seinfeld, J. H., "Homogeneous Nucleation by Continuous Mixing of High Temperature Vapor with Room Temperature Gas," Aerosol Sci. Tech., 6, 15-27, 1987.

Warren, D. R., Okuyama, K., Kousaka, Y., Seinfeld, J. H., Flagan, R. C., "Homogeneous Nucleation in a Supersaturated Vapor Containing Foreign Seed Aerosol," J. Colloid Interface Sci., 116, 563-581, 1987.

Kreidenweis, S. M., Flagan, R. C., Seinfeld, J. H., "Evaporation and Growth of Multicomponent Aerosols and Laboratory Applications," Aerosol Sci. Tech., 6, 1-14, 1987.

*Graduate Student, Chemical Engineering

**Graduate Student, Environmental Engineering Science

STUDIES OF THERMODYNAMICS, TRANSPORT, AND REACTION PROCESSES IN AEROSOL PARTICLES

Investigators: Gideon Sageev-Grader*, Mark Cohen*, Chak Chan*,
Richard C. Flagan, John H. Seinfeld**

Support: Environmental Protection Agency, Department of Energy

Heterogeneous atmospheric reactions in aerosol particles contribute significantly to the overall chemistry of SO₂ in the atmosphere. The study of these reactions under atmospheric conditions is complicated by the influences of transport and mixing processes, particle deposition, and gas-phase reaction chemistry. Aerosols, fogs, and clouds that participate in heterogeneous reactions in the atmosphere are typically aqueous, or have an aqueous layer around a solid core. Small aqueous particles rapidly equilibrate with the water vapor in the surrounding atmosphere. Two systems have been used for the study of such particles. A continuously stirred aerosol reactor has been used to study the influence of manganese-catalyzed oxidation of SO₂ on the growth of submicron-sized aqueous particles under simulated atmospheric conditions.

The levitation of single-micron-sized particles in the electrodynamic balance, a modern version of the Millikan oil-drop experiment, is being exploited in the study of a number of aspects of the behavior of small particles. The rapid equilibration of aqueous solutions with water vapor in the surrounding atmosphere allows water activities to be measured directly in particles containing a small and known mass of salt. Because the small particles are levitated without contact with foreign surfaces, supersaturated solutions can be maintained and studied. Water activities have been measured over a number of single- and mixed-salt solutions, and the kinetics of salt crystallization has been examined using single-particle experiments. A method for the spectroscopic examination of small aqueous particles has also been developed. Basically, the particle is illuminated with the output of a Michelson interferometer. Absorption of infrared radiation heats the particle and causes a small change in particle size that is detected by the scattering of visible light. By this means, the Fourier transform of the infrared absorption spectrum of particles weighing as little as 10⁻¹¹gm has been obtained.

Raman spectroscopy has also been explored for single particle analysis. Mie resonances complicate the analysis by making the intensity of the Raman-shifted radiation a highly nonlinear function of particle size. Semiquantitative composition information has been obtained, however, by comparing the Raman lines of the species of interest, e.g., nitrate, with those of the solvent, i.e., water. Resonances in the scattered radiation limit the precision with which concentrations can be determined, although the time resolution is much better than the FTIR method.

Publications:

Sageev-Grader, G., Arnold, S., Flagan, R.C., Seinfeld, J.H., "Fourier Transform Infrared Spectroscopy of a Single Aerosol Particle," J.Chem.Phys. **86**:5897-5903 (1987).

Cohen, M.D., Flagan, R.C., Seinfeld, J.H., "Studies of Electrolyte Solutions Using the Electrodynamic Balance. I. Water Activities for Single Electrolyte Solutions," J.Phys.Chem. **91**:4563-4574 (1987).

Cohen, M.D., Flagan, R.C., Seinfeld, J.H., "Studies of Electrolyte Solutions Using the Electrodynamic Balance. II. Water Activities for Mixed-Electrolyte Solutions," J.Phys.Chem. **91**:4575-4582 (1987).

Cohen, M.D., Flagan, R.C., Seinfeld, J.H., "Studies of Electrolyte Solutions Using the Electrodynamic Balance. III. Solute Nucleation." J.Phys.Chem. **91**:4583-4590 (1987).

*Graduate Student, Chemical Engineering

**Louis E. Nohl Professor, Division of Chemistry and Chemical Engineering

SCANNING ELECTRICAL MOBILITY SPECTROMETER

Investigators: Shih-chen Wang*, Richard C. Flagan

Support: Coordinating Research Council

The measurement of particle size distributions using the migration of velocities of charged particles in an electric field has been the traditional method for the characterization of particles smaller than $0.1 \mu\text{m}$. Until recently, the electrical aerosol analyzer has been the major instrument of this type, allowing measurements to be made resolving four size intervals per decade of particle diameter by a succession of measurements at different field strengths over several minutes. A higher resolution instrument, the differential mobility analyzer has recently come into use. To take advantage of its potential resolution of 5-10% on diameter requires much longer sampling times, however. Measurements can again be made in several minutes by limiting the number of size intervals sampled.

We have developed a new instrument called the Scanning Electrical Mobility Spectrometer. Rather than changing the electric field in discrete steps, the electric field is scanned continuously. The particles are classified in a time-varying electric field. For an exponential range in the field strength, there is a one-to-one correspondence between the time a particle is detected and its electrical mobility. Since the dead time associated with purging the analyzer between steps is eliminated, complete scans of as many as 100 mobility intervals can be made in 30 seconds.

Publication:

Wang, S.C., and Flagan, R. C., "Scanning Electrical Mobility Spectrometer." *Aerosol Sci. and Technol.* 13:230-240 (1990).

*Graduate Student, Environmental Engineering Science

DYNAMICS OF AGGREGATE AEROSOLS

Investigators: Steven N. Rogak*, Richard C. Flagan

Support: Department of Energy, International Fine Particle Research Institute

The theory of aerosol particle formation and growth is well established for spherical particles, but many systems produce particles with more complex structures. Fume particles formed in high temperature systems are often agglomerates composed of many smaller particles. They form when smaller particle undergoing Brownian motion collide with one another and stick together at temperatures far below the melting point of the material involved. Because the interiors of the particles are shielded by the dendritic structures that develop by successive generations of deposition, the densities of the particles decrease with increasing size. The structures of such low density agglomerates appear to be determined by the formation mechanism and to be relatively independent of the materials involved. They have been characterized as fractal structures, and numerous efforts have been made to infer formation mechanisms from analysis of the particle structure. We are investigating the fundamental mechanisms of aggregate formation and growth through direct measurements of the aerodynamic forces acting on aggregate particles, image analysis of electron microscope pictures for structure characterization, and studies of the structural rearrangements that take place due to solid state diffusion and sintering.

This is a preliminary report of work in progress, and as yet no written reports are available for distribution.

*Graduate Student, Environmental Engineering Science

TRANSFORMATIONS OF INORGANIC COAL CONSTITUENTS IN COMBUSTION SYSTEMS

Investigators: Xiaoming Li*, Steve Rogak*, Richard C. Flagan

Support: U. S. Department of Energy, on subcontract from Physical Sciences, Inc.

Mineral matter in coal undergoes a number of physical and chemical transformations during combustion, leading to the formation of ash particles with a spectrum of sizes, physical structures, and chemical compositions. The particles are an important part of the air pollution burden associated with coal combustion, and also significantly influence boiler operation by degrading the heat transfer surfaces in the boiler. Previous studies have shown that a small fraction of the ash vaporizes during combustion and later condenses to form very small particles due to homogeneous nucleation. The quantities of such fume particles are, however, not well known due to an incomplete understanding of the volatilization mechanisms. The number concentrations, sizes, and physical structures of the particles are not well described by present theories of aerosol dynamics since, in contrast to the assumptions on which aerosol dynamic models are generally based, the particles do not coalesce immediately upon coagulation. Instead, chain agglomerate particles are formed. A theoretical and experimental study of the formation and evolution of the ash fume is being undertaken to address these fundamental questions. Model systems are being used to eliminate the complexities in describing the thermochemistry of vaporizing mineral matter. Volatilization studies aimed at determining the extent to which thermodynamic equilibrium is appropriate are being conducted using well characterized mineral systems in controlled atmospheres. For the study of nucleation and aerosol dynamics, mineral vapors are being generated from gaseous precursors to assure well defined initial conditions in the experimental studies. The coalescence of agglomerate particles is being studied by exposing particles generated in one system to a controlled environment in a separate system under conditions where additional coagulation will not take place.

Publication:

Rogak, S.N., and Flagan, R.C., "Stokes drag on self-similar clusters of spheres," *J. Colloid Interface Sci.* 134(1):206-218 (1990).

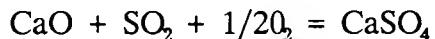
*Graduate Student, Environmental Engineering Science

COMBUSTION OF CALCIUM EXCHANGED COALS

Investigators: P. K. Sharma*, M. Khairul Alam**, Richard C. Flagan,
George R. Gavalas***

Support: Department of Energy

An alternative to the scrubbing of sulfur dioxide from combustion products is to introduce a sorbent into the flue gases. The sorbent and captured sulfur oxides could then be collected with particle-removal equipment. When sorbent particles such as lime or limestone are injected separately into the combustion chamber, sulfur capture efficiencies are generally low. An alternative approach is to introduce the sorbent directly into the carbon matrix. Two calcium impregnation techniques have been investigated: (i) ion exchange; and (ii) calcium precipitation. The former technique is an established technique for titrating carboxylic and phenolic groups in coal and has been employed as a means of calcium addition for in situ sulfur emissions control in coal combustion. The latter technique, developed under this program, involves adsorbing carbon dioxide into the coal, and then infusing the coal with a calcium acetate solution. The pH change that occurs when the CO_2 desorbs leads to the formation of calcium carbonate which precipitates within the porous microstructure of the coal. In combustion, the calcium forms CaO , which can react with SO_2 and O_2 to form CaSO_4 , or with sulfides to form CaS . Initial experiments indicated that, in oxidizing atmospheres, most of the sulfur capture occurred by the reaction with SO_2 , even though the atmosphere within the porous microstructure of the burning char is highly reducing. The equilibrium constant for the reaction



decreases with temperature so that the equilibrium sulfur retention does not become significant until the temperature drops below 1400 deg K. The reaction rate, on the other hand, decreases with temperature so that the temperature range for favorable sulfur capture is roughly 900 - 1400 deg K. The observed sulfur capture in drop tube combustion experiments increased with residence time and oxygen content. The strong effect of oxygen cannot be fully explained by the reaction equilibrium. Rather, the high oxygen concentrations lead to high temperatures of the burning char particles. At the high temperatures, calcium is volatilized and forms a fine fume that acts as a very high surface area sorbent when the combustion products cool to the point that the sulfur capture reaction is favorable.

Publications:

Sharma, P. K., Gavalas, G. R., Flagan, R. C., "Calcium Pretreatment of Coal for Sulfur Emissions Control in Combustion," Fuel, 66, 207-209, 1987.

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**Graduate Student, Mechanical Engineering

***Professor, Division of Chemistry and Chemical Engineering

KINETICS OF COAL CHAR COMBUSTION

Investigators: Yiannis A. Levendis*, Ranajit Sahu**, Paul S. Northrup***,
George R. Gavalas****, Richard C. Flagan

Support: Department of Energy

When coal is introduced into a furnace, it pyrolyzes, releasing volatile organics that burn by homogeneous gas-phase reactions and leaving behind a carbonaceous residue that must burn by gas-solid reactions. The char oxidation phase of coal combustion determines the overall combustion efficiency and directly influences many of the pollutant emissions. Reported char oxidation rates vary over many orders of magnitude depending on the coal type and pyrolysis conditions. This program has focussed on resolving the causes of that variability.

Chars are highly porous materials. Oxidation reactions take place both on the exterior surface and within the pore volume. The rate of oxidation is determined by surface reaction kinetics and diffusional resistances of the porous structure, and by catalytic effects of included mineral matter. Experimental investigations of char combustion have included experiments with a variety of coal-derived materials and with synthetic chars designed to eliminate the variability inherent in natural materials. The latter chars were mineral-free, uniformly-sized, spherical particles of glassy carbon treated to control porosity. Calcium was added to some of these materials to probe its catalytic influence on reaction kinetics. Through detailed analysis of the porous microstructures of the natural and synthetic chars and theoretical investigations designed to distinguish between diffusional influences and reaction kinetics, it was found that a single reaction rate expression describes the oxidation kinetics of those chars for which mineral catalysis is not important. Thus, physical characterization of the chars is the key to understanding its combustion behavior.

Publications:

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Levendis, Y.A., Nam, S.W., Lowenberg, M., Flagan, R.C. and Gavalas, G.R., "Catalysis of the Combustion of Synthetic Char Particles by Various Forms of Calcium Additives," *J.Energy and Fuels.* **3**:28-37 (1989).

Levendis, Y.A., Sahu, R., Flagan, R.C. and Gavalas, G.R., "Post-ignition transients in the combustion of single char particles," Fuel **68**:849-855 (1989).

Levendis, Y.A. and Flagan, R.C., "Synthesis, Formation and Characterization of Micron-Sized Glassy Carbon Spheres of Controlled Pore Structure," Carbon **27**(2):265-283 (1989).

Sahu, R., Northrop, P.S., Flagan, R.C. and Gavalas, G.R., "Char Combustion: Measurement and Analysis of Particle Temperature Histories," Combust.Sci. and Tech. **60**:215-230 (1988).

Sahu, R., Flagan, R.C. and Gavalas, G.R., "Discrete Simulation of Cenospheric Coal-Char Combustion." Combust. and Flame **77**:337-346 (1989).

Sahu, R., Levendis, Y.A., Flagan, R.C. and Gavalas, G.R., "Physical properties and oxidation rates of chars from three bituminous coals," Fuel **67**:275-283 (1988).

*Graduate Student, Environmental Engineering Science

**Graduate Student, Mechanical Engineering

***Graduate Student, Chemical Engineering

****Professor, Chemical Engineering

SMOG CHAMBER STUDIES OF HYDROCARBON OXIDATION AND AEROSOL FORMATION

Investigators: Suzanne Paulson*, Spyros Pandis**, Shih-Chen Wang*, Fangdong Yin**, Daniel Grosjean***, Richard Flagan, John Seinfeld****

Support: Coordinating Research Council, National Science Foundation, Switzer Foundation

Hydrocarbons released into the atmosphere from both anthropogenic and natural sources undergo photochemical transformations that produce ozone and other products, as well as condensable vapors. The condensable vapors form aerosol by condensation on existing particles, or by homogeneous nucleation. Three projects are being carried out in Caltech's outdoor smog chamber facility, studying key hydrocarbons under controlled conditions designed to model the polluted urban atmosphere. One project involves trying to establish an aerosol formation threshold based on hydrocarbon size and attempts to close some key gaps in hydrocarbon chemistry for long-chain alkanes and alkenes. The second project involves the critical area of biogenic (e.g., from natural sources) hydrocarbon oxidation, and has established concentration thresholds for two important biogenics: isoprene and β -pinene. The third study in the smog chamber facility examines atmospheric oxidation and aerosol formation of dimethyl sulfide and dimethyl disulfide, both of which are central to gas-phase chemistry and aerosol loadings in the clean troposphere. A battery of analytical techniques are employed in these experiments, including newly acquired Mass Spectral analysis of gas-phase samples, and tandem differential mobility analyzers for aerosol samples.

Publications:

Wang, S.-C., Paulson, S., Grosjean, D., Flagan, R., Seinfeld, J., "Aerosol Formation in Atmospheric Mixtures," Final Report to Coordinating Research Council Project No. AP-6, December 1989.

Yin, F., Grosjean, D., Seinfeld, J., "Atmospheric Photooxidation of Dimethylsulfide and Dimethyldisulfide, Part I: Mechanistic Development," submitted for publication.

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INORGANIC CONSTITUENTS OF URBAN AIR POLLUTION AEROSOLS

Investigators: Anthony S. Wexler*, John H. Seinfeld**

Support: State of California Air Resources Board

Inorganic chemical species such as ammonium, sodium, nitrates, sulfates, and chloride comprise 25% to 50% of urban atmospheric aerosols. Sodium is primarily emitted into the air mass as sea salt before it is advected over land. Chloride comes from both sea salt and direct emissions over land. Sulfates and nitrates are formed by gas phase photochemical reactions and sulfates may also be formed by heterogeneous reactions in clouds or fogs. Ammonia is primarily emitted from bacterial action in the soil and from animal husbandry operations.

In California and elsewhere around the country, critical and expensive decisions will be made in the next few years to meet federal and local standards of suspended particulate matter (PM_{10}). Models of the atmosphere over urban areas are used to develop cost effective pollution control strategies, but in order for these models to accurately predict the size and composition of aerosol particles, the basic physics and chemistry that describes the inorganic portion of aerosol particle formation must be identified and described.

Recently, we determined that the assumption of chemical equilibrium between the gas and aerosol phases does not always hold and usually does not permit prediction of the size distribution of condensate. In addition we have derived from basic thermodynamic considerations, the temperature and composition variations of the deliquescence point (the relative humidity where the particle changes from a solid to an aqueous solution). These processes and others are being integrated into the CIT-AERO, the Caltech urban aerosol model.

Publications:

Pilinis, C., Seinfeld, J. H., "Development and Evaluation of a Eulerian Photochemical Gas-Aerosol Model," Atmospheric Environment, v. 22, pp. 1985-2001, 1988.

Wexler, A. S., Seinfeld, J. H., "The Distribution of Ammonium Salts among a Size and Composition Dispersed Aerosol." Atmospheric Environment 24A, 1231 , 1990.

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DEVELOPMENT OF A STATE-OF-THE-ART URBAN ACID DEPOSITION MODEL

Investigators: Spyros N. Pandis*, John H. Seinfeld**

Support: State of California Air Resources Board

Acid deposition in forms other than rain is relatively more important in California than in other parts of the country. Ambient concentrations of nitric acid in California are roughly twice those in the eastern U.S. resulting in high rates of dry acid deposition. At the same time highly acidic fogs have been reported in the South Coast Air Basin of California with pH values as low as 1.7. In these fogs concentrations of anions and cations such as SO_4^{2-} , NO_3^- , and NH_4^+ were higher by one to two orders of magnitude than in precipitation in the same areas.

Mathematical models will eventually be a major tool in our effort to understand and ultimately control acid deposition. Three different aqueous-phase modules have been developed to describe the physiochemical processes associated with the aqueous phase in the atmosphere. These modules correspond to different levels of approximation, constitute the central core of an urban-scale acid deposition model and can be incorporated into an Eulerian three dimensional grid-based system. They include descriptions of gas-phase chemistry, aerosol formation, formation and evaporation of cloud or fog droplets by condensation of water vapor on aerosol particles, scavenging of gaseous species by water droplets and dry and wet deposition mechanisms as the ultimate models of delivery of acidity to the earth's surface.

Publications:

Pandis, S. N., Seinfeld, J. H., "Sensitivity Analysis of a Chemical Mechanism for Aqueous-Phase Atmospheric Chemistry." *J. Geophys Res.*, 94, 1105-1126, 1989.

Pandis, S. N., Seinfeld, J. H., "Mathematical Modeling of Acid Deposition Due to Radiation Fog." *J. Geophys. Res.*, 94, 12911-12923, 1989.

Pandis, S. N., Seinfeld, J. H., "Development of a State-of-the-Art Deposition Model for the South Coast Air Basin of California," Final Report to the State of California Air Resources Board, 1989.

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Pandis, S. N., Seinfeld, J. H., "On the Interaction between Equilibration Processes and Wet or Dry Deposition." *Atmospheric Environment*, 24A, 2313, 1990.

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MATHEMATICAL MODELING OF CHEMICALLY-REACTING PLUMES

Investigators: Panagiotis Georgopoulos*, John H. Seinfeld

Support: State of California Air Resources Board, William and Flora Hewlett Foundation

A new comprehensive model for chemically-reacting plumes has been developed. The model accounts for the effects of incomplete turbulent macro- and micro-mixing on chemical reactions between plume and ambient constituents. This "turbulent reacting plume model" is modular in nature, allowing for the use of different levels of approximation of the phenomena involved. The core of the model consists of the evolution equations for reaction progress variables appropriate for evolving spatially-varying systems. The equations estimate the interaction of mixing and chemical reaction, and require input parameters characterizing internal plume behavior such as relative dispersion and fine-scale plume segregation. The model offers the opportunity for calculating the evolution of chemically-reacting species in real atmospheric plumes and will be applied to the problem of predicting NO₂ levels downwind of strong point sources of nitric oxide.

Publications:

Georgopoulos, P. G., Seinfeld, J. H., "Nonlocal Description of Turbulent Dispersion," Chem. Eng. Sci. 44:1995, 1989.

Georgopoulos, P. G., Seinfeld, J. H., "Estimation of Relative Dispersion Parameters from Atmospheric Turbulence Spectra." Atmospheric Environment, v. 22, pp. 31-41, 1988.

Georgopoulos, P. G., Seinfeld, J. H., "Three-Dimensional Behavior of Mixing-Limited Chemistry in the Atmosphere," (Discussion) Atmospheric Environment, 21:2262, 1987.

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Georgopoulos, P. G., Seinfeld, J. H., "Mathematical Modeling of Turbulent Reacting Plumes: II. Application to the NO-NO₂-O₃ System." Atmospheric Environment, v. 20, pp. 1809-1818, 1986.

Georgopoulos, P. G., Seinfeld, J. H., "Instantaneous Concentration Fluctuations in Point Source Plumes," AICHE Journal, v. 32, pp. 1642-1654, 1986.

E. RISK ASSESSMENT AND REGULATION

RISK ASSESSMENT IN THE NUCLEAR POWER INDUSTRIES

Investigator: Jeffrey A. Dubin

Support: Exxon Education Foundation

Collaborative work with Professor Geoffrey Rothwell of Stanford University on risk assessment in the nuclear power industries has yielded two papers, "Safety at Nuclear Power Plants: Economic Incentives under the Price-Anderson Act and State Regulatory Commissions," and "Subsidy to the Commercial Nuclear Power Industry Through the Price-Anderson Liability Limit."

Safety at Nuclear Power Plants: Economic Incentives under the Price-Anderson Act and State Regulatory Commissions

The Price-Anderson Act has indemnified the commercial nuclear power industry since its inception. This study proposes a present value model of firm investment in reactor safety systems to investigate the safety incentives of the 1988 amendments to the Act. While the amendments increase safety incentives for electric utilities through insurance regulation, safety behavior depends crucially on the anticipated reaction of the state regulatory commission after a reactor accident.

Subsidy to the Commercial Nuclear Power Industry through the Price-Anderson Liability Limit

This study finds between 1959 and 1982 the Price-Anderson Act limited the liability of nuclear power plant operators for accidental damages to \$560 million. This limit grew to \$7 billion with the 1988 amendments to the Act. Using insurance premiums charged for the first \$160 million of coverage and the Nuclear Regulatory Commissioner's estimate of the probability of a worse-case loss, we model the distribution of c/damages with a log-logistic density function. This study finds the Price-Anderson subsidy was \$60 million per reactor year before 1982, but dropped to \$22 million with the 1988 amendments.

Publications:

Dubin, J. A., Rothwell, G. S., "Subsidy to the Commercial Nuclear Power Industry Through the Price-Anderson Liability Limit," Contemporary Policy Issues, v. 8, no. 3, July 1990.

Dubin, J. A., Rothwell, G. S., "Risk and Reactor Safety Systems Adoption," Journal of Econometrics, v. 42, no. 2, October 1989.

COMMON KNOWLEDGE IN MODELS OF INFORMATION AGGREGATION AND LEARNING

Investigators: Richard D. McKelvey and Talbot R. Page

Support: National Science Foundation

In this research, we investigated the process by which information is utilized in situations where individuals have access to both private and public information. Consider a situation in which individual economic agents obtain private information about the likelihood of some event (such as the likelihood some chemical is toxic). The agents are then periodically required to make decisions based on their beliefs (like how much of the chemical to produce or sell), and some function of these decisions (like a market price) then becomes public information. In previous research, we found conditions which guarantee that individual economic agents in the above setting, starting with different private information about an event, will eventually come to share common beliefs about the likelihood of that event. This research investigated the extent to which our earlier results can be generalized, and the degree to which the game theoretic model underlying the analysis, which assumes a kind of super rationality on the part of the agents, is a good model of real behavior. In this connection, we did both theoretical work and experimental work. The research has potential applications to risk assessment, and to research and development in competitive industries.

Publications:

McKelvey, R. D., Page, R. T., "Common Knowledge, Consensus, and Aggregate Information," *Econometrica*, 55, pp. 109-127, 1986.

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List, E. J., In: Handbook of Groundwater Development, Chapters 7, 9 and 13 (ed. Roscoe Moss Company), Wiley, 1990.

Omatu, Sigeru and Seinfeld, John H. Distributed Parameter Systems: Theory and Applications. Oxford University Press, Oxford, 430 pp., 1989.

CONFERENCES, 1987-89

Conference on Photochemical Modeling as a Tool for Decision Makers,
Ramo Auditorium, Caltech, February 1-3, 1988.

Support: Air Resources Board, William and Flora Hewlett Foundation

In February of 1988, Caltech's Environmental Quality Laboratory and the State of California Air Resources Board co-hosted a major conference on the use of air quality models for air pollution control. This was the first conference on this subject and was attended by 256 persons from industry, government, academia and the press. The goal of the conference was to bridge the gap between scientists who develop these advanced air quality models and the decision makers in the state and federal governments who must use them to form legislation on air pollution abatement. This conference brought together virtually all the principal scientists in the field with decision makers from the Air Resources Board and the US E.P.A. Prof. John Seinfeld was the Caltech co-chairman.

Publication: Conference on Photochemical Smog Modeling as a Tool for Decision-Makers, Feb. 1-3, 1988 -- Graphics Package, EQL Report No. 26, 296 pp.

