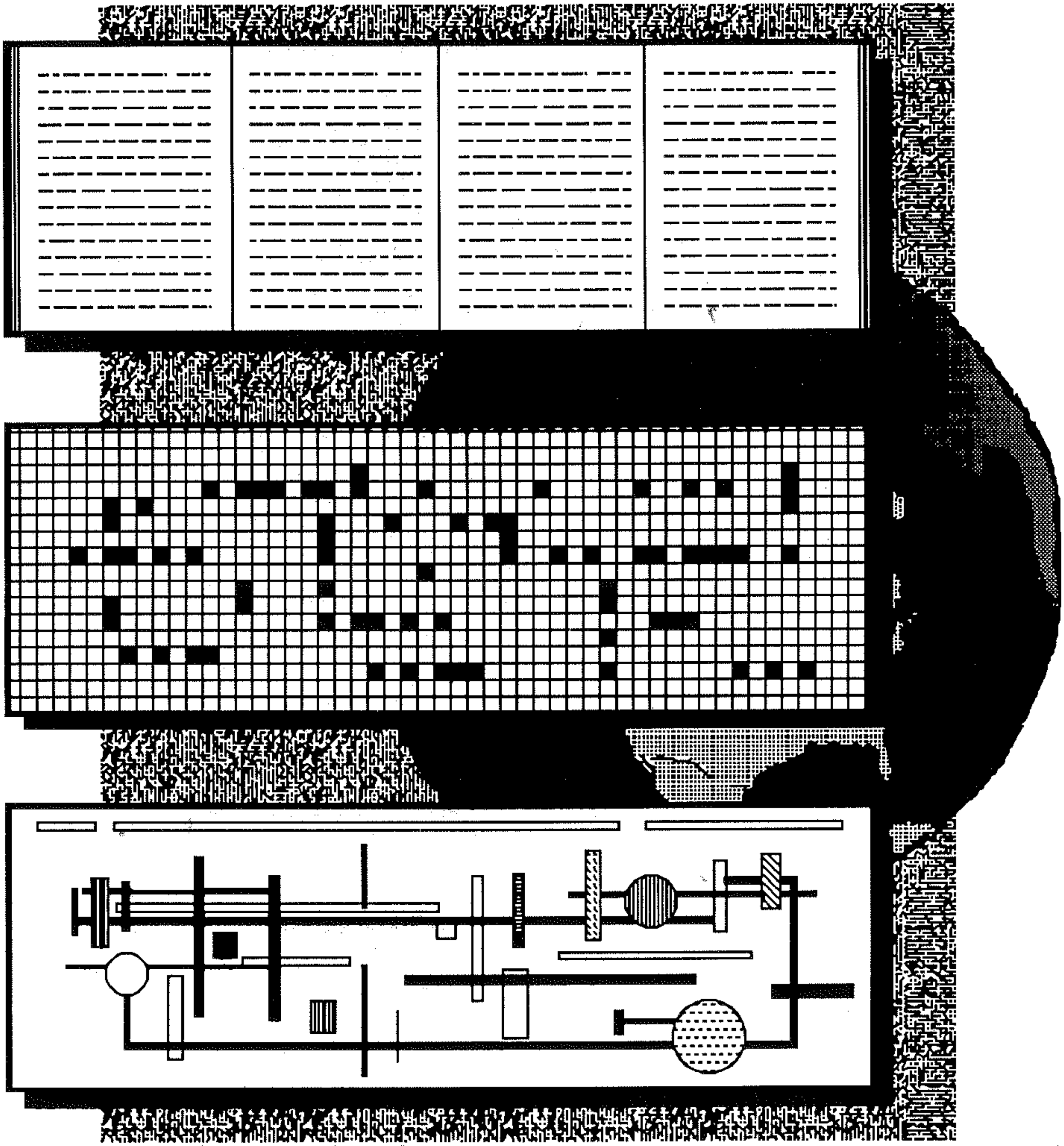
CONFERENCE ON:

FUNDAMENTAL RESEARCH DIRECTIONS IN ENVIRONMENTAL ENGINEERING

ASSOCIATION OF ENVIRONMENTAL ENGINEERING PROFESSORS



Richard G. Luthy and Mitchell J. Small, Editors

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Conference on
Fundamental Research Directions in
Environmental Engineering

November 13-15, 1988
Arlington, Virginia

Richard G. Luthy and Mitchell J. Small, Editors

Department of Civil Engineering
Carnegie Mellon University
Pittsburgh, Pennsylvania 15213

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Conference Co-Chairs:	James J. Morgan California Institute of Technology
	Charles R. O'Melia The Johns Hopkins University
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Conference Assistance:	Mitchell J. Small Carnegie Mellon University

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Fundamental Research Directions in Environmental Engineering

Conference Overview and Summary

Richard G. Luthy
Conference Chairman

Department of Civil Engineering
Carnegie Mellon University
Pittsburgh, Pennsylvania 15213

This volume contains the prepared papers and discussions that were presented at a conference organized by the Association of Environmental Engineering Professors (AEEP) on Fundamental Research Directions in Environmental Engineering. The purpose of the conference was to explore research needs and approaches for managing and controlling environmental problems from a multimedia, multidisciplinary perspective. The conference was held at Arlington, Virginia, November 13-15, 1988, and was sponsored by the National Science Foundation (NSF) with supplemental support from the United States Environmental Protection Agency (EPA).

Conference Objectives

The objectives of the conference were threefold: (1) to identify long-term directions in environmental engineering research as seen by engineers and scientists actively engaged in this research; (2) to promote an exchange of ideas between researchers studying environmental problems from different disciplinary perspectives; and (3) to promote the dissemination of the results of the conference to researchers, practitioners, professional societies, private sponsors, and granting agencies.

In presenting the results of the AEEP Conference, this volume outlines a comprehensive approach to environmental engineering/science research. The conference proceedings provide research assessments of environmental problems involving land, water, and the atmosphere utilizing physical, chemical, biological, and engineering expertise. It is hoped that these proceedings will stimulate ongoing examination of research agendas and methodologies and provide a basis for identifying significant research themes and directions into the next century. In this manner the conference can impact environmental engineering and science research and education, and the selection of research directions and priorities by sponsor groups.

Background

The first conference of this type to occur in recent years took place in December 1977 and was entitled "Fundamental Research Needs for Water and Wastewater Treatment Systems". The conference, organized by the Association of Environmental Engineering Professors (AEEP) and supported by NSF, was directed towards identifying long term research needs for water and wastewater treatment systems. A second conference of similar title was organized by AEEP and supported by NSF, and held in December, 1982. The scope of the conference was expanded to include the fate of pollutants in the natural environment, including surface water and ground water systems.

This third conference follows the second by a period of six years. Important environmental legislation has been enacted in this interval focusing on toxic and hazardous wastes, and there has been a significant increase in public awareness and concern for a wide array of environmental problems. This conference is wider in scope than the two previous meetings; the subject focus is not restricted to water and wastewater treatment systems and natural aquatic environments; rather, it is directed towards all aspects of the water, air, and land environments. The conference includes, for the first time, significant contributions from the community of air pollution scientists and engineers. It also includes researchers from the diverse fields of microbiology, fluid mechanics and social-decision sciences. The conference addresses pollutant emissions, flow through the environment, and subsequent effects, as well as the link between environmental science issues and policy questions.

Significance

While the traditional division of environmental engineering education, research and practice into water, air, and soil specialties has been successful and valuable, the critical problems challenging environmental professionals today have stimulated research which recognizes that pollution problems must be approached from a multimedia, multidisciplinary perspective. Environmental control strategies for conservative compounds (e.g. lead) or for slowly degradable substances (e.g. trichloroethylene or DDT) must be formulated from the perspective that removal from one medium results in its introduction into another. Further, control strategies for a single medium often result in trade-offs between pollutant form and concentration, in combination with spatial and temporal effects. This is evident, for example, in the complex interactions between automotive emission and photochemical smog. For these reasons, a particular focus of the conference is on multimedia approaches and comprehensive strategies for safe-guarding the environment.

The multidisciplinary focus of the conference recognizes the fact that environmental engineering and science has always utilized perspectives and tools from a wide range of disciplines, including physical chemistry, fluid dynamics, aquatic biology, public health, and meteorology. Focused research in areas such as water and wastewater treatment, air pollution meteorology, soil microbiology and groundwater geohydrology has allowed for significant progress and success in the past decades. As we continue to be faced with environmental problems that transcend single disciplines, however, a broad-based, integrated approach is required. In addition, new disciplines and expertise that can impact our approach to environmental problems continue to emerge. Examples of these include the developments in biotechnology and genetic engineering, the study of global geochemical cycles, the introduction of high-speed computers and new problem solving approaches such as expert systems, and the evaluation of societal risks and social decision making. There is a need for innovative progress in each of the disciplines which contribute to environmental engineering and science, as well as a need for a better mutual understanding and ability to integrate across disciplines.

In consideration of the interests of the Conference sponsors, it is appropriate to comment on the relevance of research in environmental sciences and engineering to the competitive position of industrial nations. Certainly it is possible for environmental research to uncover environmental problems and provide a basis for legislation and other actions that increase business costs. However, the desire for environmental quality is present in all technologically advanced countries, and increasingly in developing countries as well. Thus with respect to environmental quality, there is no *a priori* basis for assuming that the protection of environmental quality and human health results in disparate economic competitiveness among different nations. In addition, it is now apparent that some of the most critical environmental problems transcend national boundaries, with global impacts. It is thus recognized that environmental research can (1) provide all people of the world with a better and safer environment, (2) permit improved use of scarce environmental resources thereby lowering costs, and (3) lead to new, more efficient and cost-effective technologies. These latter benefits are real and attainable, and the conference attendees were asked to speak to these matters. In as much as most of the conference participants are from the academic research community, we were also asked to consider how results from the research "producers" may be transmitted to research "users" in a timely and effective manner. In this way the research community can help to both formulate national policy for environmental management and hasten technological innovation for effective control processes.

Conference Program

The conference was organized into four sessions: Physical Processes, John H. Seinfeld, Chairman; Chemical Processes, Philip C. Singer, Chairman; Biological Processes, C.P. Leslie Grady, Jr., Chairman; and Multiphase Systems, Perry L. McCarty, Chairman. Each session included three main presentations on air, land and water (the air presentation in the Biological Processes session focused on risk assessment and toxicology, and the Multiphase Systems session included a fourth presentation on social systems). Each presentation was followed by a prepared discussion. An attempt was made to select the presentors and discussants to represent both well-established researchers in the field, as well as younger, new contributors to environmental science and engineering. James J. Morgan was the conference rapporteur and provided an overall summary of the deliberations. A list of the conference programs and presentations is provided in the Appendix.

James J. Morgan aptly summarized the major themes of the conference when he noted that we now study a wider range of environmental processes than ever before - over a wider range of spatial and temporal scales and with a wider range of disciplinary skills. Our desire to obtain a deeper understanding of environmental processes and systems draws us outward, seeking knowledge from the fundamental physical, chemical, biological and social sciences. Still, the need to solve pressing, interrelated environmental problems, pulls us together, as a community of environmental scientists and engineers. It is hoped that this conference will encourage an appreciation of the broad diversity of skills and interests among environmental researchers, as well as a unified sense of purpose and mission. The excitement generated by such a meeting, and the cross-fertilization and development of new ideas that has occurred, can only lead to deeper and more significant advances in our understanding of the environment, leading to ultimate improvements in the management and preservation of environmental quality.

Conference Sessions

The first session focused on physical processes, for which an underlying theme was that models provide the principal basis for understanding physical phenomena. Kenneth Demerjian addressed major physical processes affecting the atmospheric environment and its linkages to multi-media environmental problems. Philip Roth in discussion explained the specific issues of temporal and spatial scale and uncertainty as related to model predictions. John Wilson's paper on physical processes in the terrestrial environment focused on the importance of wetting, as broadly viewed, in the context of environmental issues affecting subsurface phenomena. Linda Abriola's discussion addressed the special problems of immiscible/miscible organic pollutant transport, and the need for integration of research efforts across disciplines and for field validation of laboratory-derived modeling approaches. Paul Roberts and Jeffrey Koseff's paper on physical processes-water emphasized the linkages between physical, chemical and biological processes, and the need for the predictive capability of accurate three-dimensional simulation models which capture hydrodynamic influences with chemical and biological processes. In discussion, Desmond Lawler expanded on a theme of Roberts and Koseff with regard to the parallelism that accompanies mathematical and experimental approaches and the analogous need for study of temporal and physical scale phenomena. In concluding discussions it was noted that it is important to test models in actual field situations and that models can be used to design effective laboratory-scale experiments and to plan larger-scale tests.

The second session addressed chemical processes. The subject of environmental chemistry and chemical processes is very broad. The paper by Michael Hoffmann details eight subject areas for research in which chemical kinetics, and multiphasic chemistry and photochemistry are common themes. Harvey Jefferies in discussion emphasized how some of these topics relate to national environmental policy. In presentation of chemical processes that occur in the land environment, William Glaze focused on chemical processes that may be used to treat soil in order to remove excess contaminants. Rene Schwarzenbach discussed the need to improve understanding of the basic processes that lead to long-term alterations of the quality of soils and aquifers. In addressing research needs for chemical processes in water, Charles O'Melia emphasized the role of organic macromolecules in aquatic systems, and the effects of these species on interfacial processes in aquatic environmental systems. Steven Eisenreich discussed the research needed to understand the speciation and physiochemical state controlling fate and biotic availability. This session showed that there is an increasing need for environmental engineers to interact with other scientists and engineers to become better versed with the thermodynamic and kinetic principle governing the speciation, partitioning, transformation, and transport fate of contaminants in the environment and processes for their control.

The session on biological processes also stressed the interrelatedness of processes occurring in the environment. Session Chairman Leslie Grady called attention to the recognition that microbial research must focus on the physical and chemical events effecting biological processes. Although biological processes certainly have an indirect impact on air quality, microbial processes do not have a significant role in air media per se. For this reason the time given to air media in the other sessions was devoted instead to the important topics of environmental risk and toxicology. Michael Gough's presentation reviewed current trends in research and policy for risk assessment for carcinogens, and the need for collaboration between engineers and biologists on these issues. Joseph Roderick's discussion referred to issues of particular concern in exposure assessment, and the opportunities for engineers to make substantive improvements in reliable data and models for exposure assessment. In the paper on biological processes in land, Alexander Zehnder described how little still is known about microbial processes in a complex soil matrix with respect to the influence of solid surfaces, the potential for microorganisms to adapt to new situations, and threshold concentrations. James Tiedje's discussion of this topic described the need for innovation in demonstrating catabotic potential and understanding rate-limiting parameters. Biological processes in water were addressed by Sandra Woods, which included remarks on the effects on microbial degradation of molecular structure, and the effects of multiple phases and alternate electron acceptors/donors. Bruce Rittmann's discussion emphasized the need for cross-disciplinary application of the tools of modern biology, chemistry, microbial ecology and toxicology, and the need to work on both conventional issues as well as the new issues of hazardous pollutants. The open discussions in this session included comments on a balanced approach to accepting risk and comments on risk assessment shortcomings. Also it was noted that there has been a shift in focus of environmental microbial research towards contaminated soil and sediments; however, there are many subtle differences between traditional aquatic microbiology and those microbial processes associated with the soil environment, specifically with regard to the role of surfaces on microbial degradation. There is need for collaboration between microbiologists and engineers in order that engineers can benefit from new techniques.

The fourth session addressed multiphase systems. In his introductory comments, Session Chairman Perry McCarty described the Earth as a multiphase system in which multiple phases play a major role in fate and effects of environmental contaminants no matter what particular phase an individual may be concerned nor the scale of that concern. Yoram Cohen reviewed principal anthropogenic processes which are not sufficiently well understood in regard to intermedia transport with the atmospheric compartment. In discussion, Ronald Hites focused on the issue of toxic organic compounds in the atmosphere with specific emphasis on the need for environmental data gathering that is based on a carefully developed plan. Donald Mackay's paper on land contamination outlined the need for fundamental multimedia research in soil systems to develop improved remediation technologies, and to understand these phenomena in the growing recognition that the prevailing atmospheric concentration of contaminants such as PCBs is controlled or buffered by soil-plant-air interactions. Philip Gschwend's discussion stressed the need for improved physical picture of soil systems to assess correctly the manner in which phases are moving relative to one another, and the need for rate data appropriate for geochemical conditions. Research strategies for multiphase systems with a focus on aquatic effects were reviewed by Jerald Schnoor; important research needs were identified as fate and effects modeling with better understanding of aquatic surface chemistry and complexation. The discussion by Christine Shoemaker addressed the need for research on the methodology associated with fate and transport model validation with extension to management models. Uncertainty and risk analysis were the topics of the last paper in this session. Talbot Page referred to the problem of communication about uncertainty being partly a problem in how individuals with different backgrounds think about uncertainty and the split between classical (e.g. analytical) and Bayesian views of probability. Mitchell Small's discussion addressed the broader question of why environmental scientists and engineers must become increasingly aware of the issues of uncertainty and risk perception. This session dealt with a range of complex environmental issues for which it is evident that progress is being made on problems not generally considered at the last AEEP research conference.

James Morgan's summary of the scope and content of the deliberations of this conference emphasized the vast temporal and spatial scales in which environmental engineers and scientists conduct their research, and the importance of interdisciplinary collaboration among researchers with necessarily very focused expertise.

Acknowledgement

The sponsorship by the National Science Foundation and the Environmental Protection Agency is gratefully acknowledged. This conference could not have taken place without the help and work of a number of individuals. James J. Morgan and Charles R. O'Melia served as co-chairs and helped formulate the conference plan and programs. The session chairs helped to select and coordinate the individual contributions and presentations. Assistance in conference coordination and the editing of this volume was provided by Mitchell J. Small. Maxine Leffard of Carnegie Mellon University helped in the administration and coordination of conference registration and planning. The final manuscripts for the proceedings were typed by Shirley Knapp, Karen Peretin, Susan Singer, and Jenny Cochran. Finally, I would like to thank the more than 150 conference attendees whose enthusiastic participation helped to make the conference a success, and whose continuing efforts make the field of environmental science and engineering so exciting and enjoyable.

Physical Processes - Introduction

John H. Seinfeld
Department of Chemical Engineering
California Institute of Technology
Pasadena, California

The first set of papers address current research issues related to physical processes in air, land, and water systems. Although the meeting was structured according to physical, chemical, biological and multiphase processes, it became evident early that environmental problems are characterized by an intimate intertwining of physical, chemical, and biological processes, frequently involving multiphase phenomena. This first session focused on physical processes, with attention given to the role of physical processes in the integrated scope of environmental problems. A theme underlying the papers in this session, and indeed most of the papers in the entire meeting, is that models are the ultimate integrators of our understanding of the phenomena occurring. These three papers and their companion discussions address major uncertainties in our knowledge of physical environmental processes, as well as the representation of these processes in environmental models.

Physical Processes - Air

Kenneth L. Demerjian
State University of New York
Albany, NY

Introduction

Physical processes play an essential role in governing the lifetimes of chemical substances in the atmosphere and are the major means by which these substances are distributed and deposited on the surface of the earth. Whether the concern is the transport and fate of a pollutant species emitted into the atmosphere or understanding the natural bio-geochemical cycles of trace chemical constituents that make up the global atmospheric environment, physical processes must be considered. The removal of atmospheric pollutants is obviously a two edged sword. On the one hand, it represents the atmosphere's natural process for cleaning itself, which benefits our health and welfare based on the quality of the air we breathe. On the other hand, the chemical contaminants that are transported and removed by precipitation and dry deposition impact our terrestrial and aquatic ecosystems in adverse ways, threatening many of our natural resources.

The following brief write-up provides a synopsis of the critical physical processes affecting the atmospheric environment and its linkages to multimedia environmental problems.

Transport and Dispersion

The distribution of chemical constituents emitted into the atmosphere is critically related to the vertical and horizontal transport. The mechanisms for vertical exchange are complex and varied, ranging from clear-air processes over various terrain and land use conditions to moist convection associated with non-precipitating clouds and cloud systems. Precipitating clouds redistribute pollutants vertically in the atmosphere, with updrafts carrying surface-based pollutants into the upper layers, and downdrafts bringing rain, cloud and interstitial air to the lower levels of the earth's surface. With regard to photochemical oxidants, non-precipitating clouds are of particular interest, since they are prevalent in the warm season and are effective in redistributing pollutants between the mixed layer and the free troposphere. The magnitude of their impact is highly variable in time and space and will depend on the cloud population, distribution, and their vertical extent. Entrainment processes within the clouds play a critical role in determining the net vertical exchange in the atmosphere. The horizontal distribution and population density of clouds are highly variable regionally, and over diurnal and seasonal time scales. Long range horizontal transport of ozone and its precursors are expected to be strongly influenced by cloud systems. As an example, experimental evidence of cloud induced vertical exchange of ozone between the mixed layer and free troposphere has recently been documented (Ching et al. 1988).

Horizontal transport of pollutants on a regional scale is controlled by the height at which emissions are released, their chemical and physical lifetimes, and horizontal dispersion. Consequently, the horizontal distribution of pollutants is strongly impacted by such factors as the speed and direction of the transport winds, vertical mixing in and between layers, presence of wind shear, extent of coupling between the mixed layer and free troposphere, surface pollutant fluxes and source distribution. The transport winds are expected to translate along isentropic surfaces, which are not necessarily horizontal. Wind shear will cause pollutant sources to undergo horizontal transport and dispersion such that the pollutants in the upper air will be redistributed in three dimensions and over greater areas than would be otherwise anticipated from surface winds. Significantly distorted horizontal patterns will develop and vary with respect to the vertical levels of the atmosphere and the varying transport and dispersion conditions.

There is a need to develop acceptable inert and reactive tracer systems for deployment in field studies which can be used to help evaluate and further develop atmospheric transport, dynamic mesoscale and synoptic scale numerical models. In addition there is need to evaluate the integration of the above modeling systems and 4-D data assimilation approaches for improving pollutant transport modeling systems. New generation meteorological remote sensing systems, soon to be deployed by the NWS as part of the National STORM program, including the wind profiler and NEXRAD networks, must be quickly assimilated for use in transport models and evaluated to determine their impact on pollutant transport model performance.

Cloud and Precipitation Scavenging

In addition to vertical transport clouds and associated precipitation also play important roles in the chemical transformation and removal of tropospheric trace species. Clouds also strongly influence the distribution of radiation in the troposphere, leading to changes in tropospheric photochemistry when clouds are present. Within cloud updrafts, surface-derived trace species are efficiently transported into higher layers of the troposphere, where temperatures are lower, photolysis rates are enhanced, and higher horizontal wind speeds can efficiently transport trace species around the globe. Laboratory studies of SO_2 oxidation show that aqueous-phase reactions between dissolved SO_2 and oxidants such as O_3 and H_2O_2 are extremely rapid, suggesting that a major fraction of emitted SO_2 is oxidized to sulfuric acid in clouds. Other important species such as HCHO, N_2O_5, and perhaps NO_3 may go through rapid aqueous chemical transformations in cloud drops. Deposition of soluble trace species in precipitation is probably the most effective sink for the end-products of sulfur and nitrogen oxidation in the troposphere: sulfuric and nitric acids; leading to the formation of acidic precipitation. The presence of clouds will strongly modify distributions of photon flux in the troposphere. Under some conditions, radiation modeling studies suggest that the upper regions of clouds contain perhaps the highest photon densities found in the troposphere, implying that intense aqueous- and gas-phase photochemistry can occur in these regions.

While the microphysics of nucleation scavenging, aqueous chemistry, and trace gas and particle scavenging by cloud and precipitation particles is relatively well documented, it is difficult to directly infer and evaluate the occurrence of these processes from cloud observations. Numerous chemical and meteorological processes influence the chemical composition of clouds and precipitation, making it difficult to validate our current understanding of scavenging processes using measurements of cloudwater composition. Because many of the cloud chemical and scavenging processes occur on small scales, it is difficult to extrapolate these effects to larger domains of interest. A comprehensive field program that is closely allied with a system of cloud chemical and microphysical models needs to be developed. Each important mechanism involved, both physical and chemical, needs to be tested through iterative intercomparisons among modeling, field, and laboratory studies. Only then can a complete understanding of the physical and chemical processes in clouds be obtained.

Dry Deposition

Dry deposition is the removal of chemical species from the atmosphere at the air-surface interface. It is of practical interest, in that this process provides a major control on the physical lifetime of a chemical substance in the atmosphere. It therefore is essential to our understanding of atmospheric cleansing processes, and equally important, it is also a major pathway for chemical exposures in terrestrial and aquatic ecosystems. The dry deposition of gaseous phase material, aerosols, and cloud droplets to surfaces is subject to a variety of chemical, physical, and biological factors. Micro-meteorological transport related phenomena, the physical and chemical properties of the depositing substances, and the nature of the surfaces exposed are important components in estimating this process. Though significant progress has been made in the measurement of the transport fluxes of chemical species to and from exposed surfaces, from which dry deposition is inferred, an effective direct measurement technique has yet to be developed. Therefore the accumulation of chemical species on forest or crop canopies and on lake or soil surfaces can now be only crudely estimated. The flux of any airborne material to a surface can be effectively considered using a resistance modeling approach, which is analog to electrical resistance. The model considers the airborne material flux as current flow in an electrical circuit; the individual resistances are associated with specified atmospheric and surface properties. These breakdown into three major components, an aerodynamic, diffusive boundary, and surface resistance. The model provides a reasonable conceptualization of the many contributing processes and allows comparisons of their relative importance. The inverse of the total resistance to transfer to a surface is equal to a deposition velocity. This convenient concept, which relates the downward flux of airborne material divided by airborne concentration to velocity of deposition at some specified height above the surface (typically 1 to 2 meters), is used to incorporate dry deposition processes into models. These approaches, though limited, represent the current state-of-the-art for incorporating dry deposition processes in atmospheric simulation models.

There is an obvious need for the development of direct surface deposition monitoring techniques. In addition, field experiments must be designed to evaluate modeling approaches to dry deposition.

References.

Ching, J.K.S., S.T. Shipley and E.V. Browell, Evidence for cloud venting of mixed layer ozone and aerosols. *Atmospheric Environment*, 22, 225-242, 1988.

Hicks, B.B., D.D. Baldocchi, R.P. Hosker, Jr., B.A. Hutchinson, D.R. Matt, R.T. McMillen, L.C. Satterfield, On the use of monitored air concentrations to infer dry deposition (1985). NOAA Technical Memorandum ERL ARL-141, Air Resources Laboratory, Silver Spring, Maryland, November 1985.

Walcek, C.J. and J.S. Chang, The role of clouds in the vertical exchange of tropospheric trace gases. *Tellus* (in press).

Discussion: Physical Processes - Air

Philip M. Roth
836 Fawn Drive
San Anselmo, California 94960

Dr. Demerjian's paper, although brief, thoughtfully addresses the major atmospheric processes requiring attention in future research endeavors. Physical processes considered include transport and dispersion, cloud and precipitation scavenging, and dry deposition. Dr. Demerjian offers six major research recommendations. Of these, three focus on the development and/or evaluation of experimental techniques for use in major field programs, two on suggestions for field programs *per se*, and one on evaluation of the predictive performance of the latest generation of regional scale meteorological models. I concur with Dr. Demerjian in his recommendations, noting that he has covered much of the "important turf".

A framework for both integrating and contemplating Dr. Demerjian's comments is regional scale air quality and deposition modeling. Were each of the six recommendations put forth to be seriously pursued, critical understanding of key processes would clearly increase, and sound, more fundamentally based formulations of regional simulation models would certainly emerge. Also, the time to application of these models with reasonable confidence would surely be shortened.

This framework is a point of departure for my comments in suggesting some additional needs, and thus research directions, in the study of physical processes. Dr. Demerjian has identified needs of the first magnitude; the eight suggestions that follow are in several cases of lesser importance, but focus on existing needs nevertheless. Principal unifying themes for these suggestions will be those of scale (temporal and spatial) and uncertainty (as related to modeling and decision making).

Pertaining to Scale

1. Developing reliable meteorological models

While Dr. Demerjian mentions the general need to further develop meteorological models, attention should be directed to specific existing needs. These include meteorological models that:

- reliably develop wind and temperature fields for input to models that estimate concentration and deposition fields on spatial scales ranging from local to regional. For urban scales and for transport into and out of rough or mountainous terrain, there is need for models that accurately treat both terrain and thermal influences. Field programs are needed to provide data for input to models under study and for use in evaluating their performance.

- estimate the distribution of expected winds over an ensemble of possible outcomes, thereby providing a means for estimating the distribution of ambient concentrations that might result from such a wind field. Such models would find use, for example, in estimating the spatial field of potential exposure to an accidental release of hazardous material in "real time", where accurate estimation of a particular realization is not possible.

Data availability can vary greatly from one situation to the next at a given spatial scale. Thus, there is need to develop a model or set of models that emphasize theory in those circumstances where supporting data are scarce or unavailable, and emphasize the use of actual data where these are available.

2. Linking models of differing spatial scale

Coarse scale, grid-based models generally cannot account for phenomena occurring at the subgrid scale. In regional modeling, for example, subgrid scale variability in the location and spatial coverage of precipitating clouds cannot be adequately represented, thereby limiting the accuracy of such models in predicting wet deposition. The ability to provide a description of the relevant dynamic processes at a finer scale, embedding this description in the coarser scale model, would be particularly attractive in this instance - as well as in a variety of other modeling situations.

Key inputs to urban scale models are upwind and aloft boundary conditions. In most situations, available data bases are inadequate for characterizing these conditions. The estimates of concentrations provided by regional scale models would be a welcome alternative for estimating boundary conditions.

Developing facile means for linking models of differing scales thus will be an important advance in atmospheric modeling. The high speeds of modern parallel processing computers will facilitate this advance. However, proper representation of relevant dynamic processes at appropriate spatial and temporal scales is still a critical element in developing "nested" systems of models, and further development of component models, as well as supporting field programs, is needed.

3. Improving the practice of performance evaluation

Advances in the practice of model performance evaluation are needed if substantive progress is to be made in diagnostic analysis (where a model appears flawed), model improvement, determination of the range of applicability of a model, and estimation of the uncertainties attending model prediction. Topics meriting attention include rendering more commensurate in spatial and temporal scale the predictions of models and the observations with which they are compared (e.g., characterizing the variability associated with point measurements and developing and applying techniques such as remote sensing for measuring at the spatial resolution of the grid); improving procedures for diagnostic analysis; advancing theory and application in the estimation, characterization, and treatment of uncertainty and variability; developing procedures for evaluating the performance of "preprocessor models" such as meteorological and emissions models; developing procedures for selecting the types, range, and number of meteorological episodes needed for adequate testing; developing techniques for determining the range in emissions levels over which a model may be reliably applied when it has (typically) been tested only over a range in meteorological conditions (and thus for various levels of "dilution" of more or less constant emissions); and developing suitable procedures for judging model performance. Clearly, model evaluation provides fertile ground for research.

4. Developing reliable estimation methods for periods of long duration

Long term (seasonal and annual) estimation of pollutant concentrations and their distributions is usually based on (1) approximate or highly simplified treatments of governing processes, or (2) more detailed modeling of "typical" episodes, followed by aggregation of episodic results using weighting based on frequency of occurrence of meteorological regimes from which the episodes were drawn. Research is needed in developing improved approaches to estimation of concentrations for periods of long duration. Needs include developing sound means for classifying episodes, aggregating and weighting the results of episodic studies, and evaluating the performance capabilities of the procedures developed.

Pertaining to Uncertainty

5. Characterizing and estimating uncertainties in model predictions

Uncertainties associated with model estimates of concentrations and deposition are typically poorly characterized. Knowledge of these uncertainties can be as important as the estimates themselves in the interpretation and use of the results. Substantive effort is needed in developing means for characterizing and estimating the uncertainties associated with the predictions of primary simulation models and supporting preprocessor models.

6. Developing means for estimating the chances of achieving an air quality goal through the adoption of a selected strategy

Decision makers would undoubtedly value more highly the results of modeling analyses if they were provided with estimates of the chances of failing to achieve an air quality target if attainment of that target is, in fact, predicted using the model. (They know that models are not as accurate as they would wish.) The thinking and methods of decision analysis should find application in linking model use with the needs of decision makers. Support for this type of research is likely to be forthcoming, as the primary potential client community is influential in determining funding.

Pertaining to Other Needs

7. Characterizing gas-to-particle conversion processes

A key element in the formation of atmospheric aerosols and acids is the conversion of gases to particles. Condensation, nucleation, particle growth, and coagulation are critical processes in the conversion. However, the dynamics of these processes are incompletely understood, largely because of the difficulties that attend appraising theoretical formulations. Carrying out the needed laboratory and observational studies is quite difficult and tedious; considerable additional research effort is needed in this field.

8. Developing source-oriented particle (PM-10) prediction models

The existence of national and state ambient air quality standards for fine particles (PM-10) and the exceedance of these standards in many geographical areas has created a need for modeling the processes leading to the formation of particles and accounting for their composition and concentration. Because of the extreme complexity of the processes influencing particle production, transport, dispersion, and deposition, and the many routes to formation of particles (which may be comprised of sulfates, nitrates, organics, elemental carbon, and crustal material), full description may appear intractable. Yet, important progress has been made in modeling processes influencing the concentration distributions of some types of particles. However, further research, including carefully planned field programs and model development, is needed if useful tools are to become available.

These suggestions are but a sampling from the spectrum of research needs in physical processes, beyond those suggested by Dr. Demerjian. I hope that they stimulate interest and thought.

The Need for Research: Physical Processes - Land

The Role of Wetting in Environmental Problems

John L. Wilson
Department of Geoscience
New Mexico Institute of Mining and Technology
Socorro, NM 87801

Background

One often ignored physical process affecting environmental engineering problems concerns the "wettability" of porous media, particularly soils. By wettability I refer to the relative affinity of the solid component of the media for fluids such as air, water or oil [see Adamson, 1982]. For example, a hydrophillic soil has an affinity for water. Rain will infiltrate into a hydrophillic soil, limited only by the soils ability to conduct water to depth [see, Letey et al., 1962]. A hydrophobic soil has a greater affinity for oil, or perhaps air, than water. A drop of water spilled on this soil will not penetrate, but will "bead up." A drop of oil will be absorbed. In examining environmental problems we often assume that the media is hydrophillic. This may not always be so, with environmental or other consequences, as the follow examples demonstrate.

- Hydrophobic soils have become a serious management problem on certain golf course putting greens around the country [Karnok et al., 1987]. By top dressing the greens with sand the soil profile becomes layered, sometimes creating high water content anaerobic conditions. This favors the growth of soil micro-organisms which deposit an organic layer, generally composed of metal sulfides, on the soil particles. Scanning electron photomicroscopy (SEM) shows that this layer may completely, or only partly cover the sand particles [Karnok et al., 1987]. The organic layer changes the hydrophillic sand to a hydrophobic sand. A variety of commercial "soil wetting agents" are available to treat hydrophobic soils. Presumably the hydrophobic end of these nonionic surfactant molecules is adsorbed by the organic coating, leaving the hydrophillic end exposed to the pore space. The net result is a more hydrophillic soil. The surfactant also reduces the interfacial (surface) tension between water and air. This reduces the capillary forces that hold water in the soil. The net result is that the "wetting agent" has both beneficial and harmful effects [Miller et al., 1975; Pelishek et al., 1962]. Using surface active agents to alter wetting often requires that competing objectives be balanced. If desorption of the surfactant can be controlled, this competition can be resolved in favor of improving hydrophillicity [Valoras and Letey, 1968]. Although golf greens are my favorite example, the problem of hydrophobic soils is much more widespread in agronomy and horticulture [see, e.g., De Bano and Letey, 1968; and abstracts in EOS <u>68</u> (44), 1296-1297, 1987].
- A recent article in the *New Yorker* discusses another problem (McPhee, 1988). To the north of Los Angeles are the San Gabriel Mountains. Because of their unique location at the junction of plate boundaries, these mountains are growing quickly, as much as 1 mm per year. Only a few miles

from the Pacific Ocean they steeply rise to over 10,000 feet in height, and are far taller relative to Los Angeles, than the Rockies are relative to Denver. The San Gabriels are eroding almost as quickly as they are growing. They generate an enormous amount of debris that is carried down the mountains by simple gravity and rainfall runoff. Over the last fifty years LA has dramatically expanded, and some of the choicest homesites are along the paths of the debris flows. In a bad year several hundred homes are lost to debris flows. One natural agent in this process in the alteration of soil wetting by "brush" fires in the chaparral along the steep hills and mountainsides [Krammes and Osborn, 1968]. The fires convert the heavy wax-like substances in the vegetative cover into an organic coating on the soil grains in a layer a few centimeters into the soil. Above this shallow hydrophobic layer, the veneer of burned soil is hydrophillic. Months later, if a series of large rainstorms come through, the water cannot infiltrate in these burn areas. The water runs off, increasing erosion, and adding to the flooding and debris flows [Krammes and Osborn, 1968; McPhee, p. 66, 1988]. Fires are artificially suppressed in the Los Angeles basin, but eventually each area accumulates enough fuel, so that when a fire gets out of control it burns hotter than it ever would naturally. The organic coating on the soil gets thicker, and penetrates deeper. The potential for floods and debris flows is greater than ever. Soil wetting agents applied after the fire offer one possible, but perhaps ineffective, mitigating strategy [De Bano et al., 1967].

- The success of crude oil recovery from petroleum reservoirs is known to depend on the preferential wetting of pore solid surfaces [see excellent review in Anderson, 1986a, 1987c]. Although it is typically assumed in reservoir engineering studies that the rock is "water wet" (hydrophillic), the field evidence actually suggests otherwise [Anderson, 1986a]. For example, Treiber et al. [1972] studied reservoir rocks from 55 oil reservoirs. Only 15 were classified as water wet. Of the rest, three were considered of "intermediate wettability" and 37 were classified as "oil wet" (hydrophobic). The degree of wettability is a function of the nature of the solid surface, the characteristics of the crude oil, and the composition of the water (brine). Hydrophillic surfaces, such as silica, are altered by the deposition of organic material that was originally in the crude oil, and/or by the adsorption of polar oxygen-, nitrogen-, or sulfur-containing compounds. Only a few of Treiber's hydrophobic reservoirs were strongly oil wet; in these rocks the solid had a bitumen coating. For each phase present in an oil reservoir, that is, for the oil and the water, wetting controls the relative permeabilities, the capillary pressure/saturation relationships, the capillary trapping of residual saturations, and the dispersivities [Anderson, 1987a,b,c; Hornof and Morrow, 1988; Morrow et al., 1973, 1973, 1986; Wang, 1988; and Wardlaw, 1980, 1982]. In short, wetting controls the oil recovery process, and should influence the design of enhanced oil recovery operations. Surfactants are seldom, if ever, used in petroleum reservoirs as "wetting agents". Their principle application is to reduce interfacial tension (IFT) between the oil and water, and thus reduce capillary forces. For sufficiently high flow rates (high 'capillary numbers') viscous forces dominate capillary forces and some of the residual oil can be mobilized and recovered [Adamson, p. 436, 1982; Chatzis, et al., 1983; Hornof and Morrow, 1988; Morrow, 1979; Taber, 1969; Wardlaw, 1980, 1982]. Because of viscous fingering, gravity overriding, or permeability heterogeneity, reservoir floods tend to follow preferred paths, by-passing large volumes of original oil or residual oil. These are referred to as "mobility" problems in petroleum engineering. Surfactant-based foams are sometimes used to control mobility. In a porous media a foam is comprised of gas bubbles separated from each other by stable liquid lamellae. The bubbles may be either continuous or discontinuous - the foam is not the "bulk" foam we encounter above ground [Ransohoff and Radke, 1988]. The foam appears to improve mobility by increasing the apparent fluid viscosity along the preferred flow paths [Fried, 1961; Treinen et al., 1985]. The flow resistance along these paths increases, and the flood is diverted elsewhere. Whenever surfactants are used to reduce IFT's or for mobility control there is the possibility that wetting will be inadvertently modified.

- The improper disposal of hazardous organic liquid waste poses a serious threat to the nation's groundwater supplies. Groundwater supplies are additionally threatened by pollution in the form of spills and leaks of petroleum hydrocarbons and other organics from storage tanks and pipelines. Many of these organic liquid pollutants have a low miscibility in water causing them to migrate as a separate phase through the subsurface. As an organic liquid moves through the subsurface, a portion of its volume is left behind as immobilized pockets of liquid, the so-called residual saturation of petroleum engineering, trapped by capillary forces within the pore space [Alberton et al., 1986; Wilson et al., 1987; Schiegg, 1980; Schiegg and McBride, 1987; Schwille, 1984, 1988].

> Eventually, the entire volume of an organic liquid spill may become immobilized by this process. Commonly, hydraulic remediation techniques - pumping out the free organic liquid phase - recover less than 50% of the original spilled volume [Wilson and Conrad, 1984]. Much of the organic liquid that is not recovered remains trapped within the porous matrix of the soil, immobilized by the effects of capillarity. Although the organic liquid phase is often only very slightly miscible with water, it is important to realize that small concentrations of the various components of the organic liquid partition to the air and water phases, even when the organic liquid has been immobilized by capillary trapping [Corapcioglu and Baehr, 1987a,b]. In effect, the organic liquid phase acts as a continuing source of dissolved and/or vaporized organic pollutants and must be removed in order to clean up a contaminated aquifer. The migration, capillary trapping, and inter-phase partitioning or organic liquids is dependent upon: the number of fluid phases present; the physical forces exerted on the fluids (pressure, buoyancy, and capillary forces); the surface chemistry (wetting properties of the system); and the soil structure and heterogeneity [Albertson et al., 1986; Wilson et al., 1988; Schiegg, 1986; Schwille, 1986, 1988]. As the golf course green, the chaparral fire and petroleum reservoir examples demonstrate, wettability of normally hydrophillic surfaces can be changed by contact with compounds present naturally in the environment. This alters the flow and sorption behavior of the porous medium. It appears likely that some of the compounds present in organic waste solutions, or even gasoline, can likewise alter wettability. Schiegg observed such changes in his laboratory study [1980], as we have in ours. The transport of the organic compound under natural conditions and the success of alternative remediation designs will be affected. To the best of my knowledge there has been no study of wettability for these types of environmental problems.

Wettability issues are sometimes addressed by environmental engineers when it comes to spill management. Absorbent materials are employed to contain, absorb, and clean-up spills, leaks, etc. Sometimes mineral (clay) particles are used, but because they are more water than oil wet, they are inefficient. Polymeric socks (often polypropylene or polyethylene) are much more efficient because they are composed of hydrophobic, oil-wet material.

Wettability issues also arise when the microbiology of a porous media is studied. The attachment of bacteria to solid surfaces is an important issue in the design of above-ground and in-situ treatment processes. In particular biofilm formation requires such an attachment, while in-situ bacteria migration into new treatment zones requires bacteria mobility [see various papers in Marsell, 1985; Pringle and Fletcher, 1983]. The degree of adhesion depends on the exposure [Corpe, 1970; Nilsson and Dostalek, 1984], surface wetting [Pringle and Fletcher, 1983; Van Loosdrecht et al., 1987b] and cell wall wetting [Van Loosdrecht et al., 1987a]. As the golf course green example demonstrates, bacteria have the ability to "condition" the soil [Baier, 1970]. A primary film of organic molecules is adsorbed to the solid surface. In marine environments these conditioning films have been analysed [Baier, 1979; Pringle and Fletcher, 1983], and for that case consist mostly of glycoproteins, proteoglycans, or humic residue end products.

Soil Wetting

Soil wetting can change, from an initially strongly ‘water wet’ hydrophillic condition, to a hydrophobic condition. The examples above illustrate that the change can be caused by physical, chemical or biological mechanisms. The major physical mechanism is heat, which deposits a coating of organic material on the soil. This has been observed in chaparral soils [De Bano et al., 1967; Krammes and Osborn, 1988] and petroleum reservoirs [Treiber et al., 1972]. The major chemical mechanism is adsorption, particularly of polar oxygen-, nitrogen-, or sulfur-containing compounds [Anderson, 1986a; Morrow et al., 1986]. The biological mechanisms, and there may be several, appear to be poorly understood.

Wetting can be altered in the laboratory by intentional chemical treatment. Organchlorosilane compounds are used in petroleum engineering and soil science to establish various levels of hydrophobicity in sandstone cores, glass bead packs and etched glass micromodels [e.g., Anderson, 1986a, 1987c]. The organosilane reacts with the silica surface leaving its organic portion exposed, thus presenting a hydrophobic surface to the pore space. Chemical modification of clays and other soils has recently been investigated, with a focus on sorption behavior by hydrophobic surfaces in aqueous media:

- Boyd et al. [1987] treated soil and clay surfaces with different alkylammonium cations of the form $[(CH_3)_3\ NR]^+$, where R was a C_{12} to C_{18} hydrocarbon. They found that organo-smectite complexes formed using hexadecyltrimethylammonium ($HDTMA^+$) were at least ten times more effective than soil organic matter in immobilizing organic toxicants such as benzene and pentachlorophenol. Bouchard et al. [1987] found that ethylhexadecyldimethylammonium ($EHDDMA^+$) quantitatively replaced exchangeable metal cations sorbed on clay minerals. Once sorbed, the $EHDDMA^+$ remained sorbed on the surface even in the presence of high concentrations of alkali or alkali-earth cations. Furthermore, the $EHDDMA^+$ remains sorbed on the surface in the presence of organic solvents [C.G. Enfield, personal communication, 1987]. The $EHDDMA^+$-treated surfaces increased sorption of neutral organic compounds from aqueous solution by up to three orders of magnitude over that observed for the untreated surfaces [Bouchard et al., 1987].
- Mortland et al. [1986] recently determined the sorption of a number of chlorine-substituted phenols on surface-altered smectite. The hydrophobicity of the clay surface was altered by the sorption of quaternary ammonium cations including hexadecylpyridinium ($HDPY^+$), $HDTMA^+$, trimethylphenyl ammonium ($TMPA^+$), and tetramethyl ammonium (TMA^+). The results of the sorption experiments indicated that some cations ($HDMTA^+$ and $HDPY^+$) yielded a strongly hydrophobic surface, while other cations ($TMPA^+$ and TMA^+ yielded a heterogeneous hydrophobic-hydrophillic surface. The sorption of the various substituted phenols from water or hexane solutions reflected their individual polarities and the hydrophobicity of the solvent vs. the hydrophobicity of the modified surface.

These surface changes were made to alter sorption behavior. It is not unreasonable to hypothesize that the altered wettability will also effect the behavior of fluids.

Wetting properties can be measured using a variety of quantitative and/or qualitative methods. In our laboratory we use three quantitative methods. Contact angles are measured on quartz crystals and treated glass plates [Adamson, 1987]. Wetting in treated or natural soils packed in columns are measured by the USBM [Donaldson et al., 1969] and Amott [Amott, 1959] methods. These methods are similar to the methods used to obtain pore pressure-saturation curves. Qualitative methods include the sessile-drop method [Adamson, 1982] on glass, and a variety of methods with soils. The imbibition method examines the propensity for spontaneous imbibition of water into an organic saturated soil and vice versa. The imbibition method is related to the Amott test. Microscopic examination involves visually examining fluid distributions under an optical microscope. Flotation methods involve shaking organic liquid, water and soil together in a glass bottle and observing the distribution of each phase after equilibrium is established. Wettability measurement methods are reviewed in Anderson [1986b] and Adamson [1982]; see also De Bano and Letey [1968]; Donaldson, et al. [1980]; and Van Loosdrecht et al. [1987a].

Wetting is often non-homogeneous. That is, wetting, can be different in different locations in the porous media. Whether it's on a pore scale, or a porous media scale, heterogeneous wetting can imply clumps of hydrophobic material, intermixed with the hydrophillic surfaces. For natural soils, the heterogeneity can be due to the original mineralogy of the soil particles. It is also caused by the non-uniform alteration of wetting of organic matter. Petroleum engineers refer to "mixed wettability" conditions, when describing media in which the large pores contain continuous oil-wet paths, while the small ones are water-wet [Anderson, 1987; Melrose, 1982; Salathiel, 1973]. The basic idea of mixed wettability may be appropriate for hazardous waste sites. Because the soil is initially hydrophillic, neither the air nor the organic phase may be unable to drain the small pores of water under gravity or capillary [Wilson et al., 1988]. The soil surfaces in these small pores may not be as readily exposed to surface altering agents. Thus the small pores remain water wet, while the large pores, containing organic liquids, are altered toward an oil wet condition. Random or speckled wettability refer to soils in which there is no interconnected or organized path for a particular wetting. Whether it's random or not, heterogeneous wetting can have a significant impact on behavior [see review in Anderson, 1987c]. The chaparral fire example, demonstrates that this can be especially so when the altered wetting is organized into layers or blocks.

Wetting alterations may occur quickly, or only over an extended period of time. Thermal alterations, such as the chaparral fires, can occur in a few minutes or several hours. Some bacterial related coatings may also occur quickly [Pringle and Fletcher, 1983]. In most examples of chemical alteration the soil must be "aged" with the organic complex; in which case the wettability is a function of exposure time [Anderson, 1986a, 1987c]. I suspect this is the case with hazardous waste and gasoline spill sites. Wetting alteration can be reversed. The chaparral soils are eventually rejuvenated, and after a few years become hydrophillic again. Rock cores from petroleum reservoirs must be carefully handled, in order not to artificially modify wettability [Anderson, 1986a, 1987c]. "Wetting agents", usually non-ionic surfactants, can be added to reverse the wettability.

Wetting alterations affect the behavior of fluids and chemicals. The golf course green and chaparral fire examples depict wetting problems resulting in too little infiltration and too much run off. The petroleum reservoir, and the hazardous waste site or gasoline spill problems, illustrate cases in which the movement of water, an organic liquid, and a gas are all affected by wettability. Also affected are the chemical partitioning between fluid phases and the solid, and diffusion/dispersion of chemicals within each fluid phase. In short, the entire transport system is influenced by the wettability. The consequences are that, without understanding wettability and its influences, there will be problems that we cannot model and for which we cannot design appropriate engineering solutions.

Research Needs

Within the context of environmental problems research is needed in several areas. This research may be primarily laboratory based or field based. Theoretical research is called for in some cases. This proposed research can use as a foundation much of the work that has taken place in other fields, in particular petroleum engineering.

- Can soil wetting be altered in the natural environment, and under anthropogenic stress? If so, how? Does wetting alteration require aging?
- Is wetting actually altered to any significant extent in the environment, or is this simply an academic problem?
- Where is wetting altered? What is the spatial pattern and heterogeneity? What does heterogeneous wetting look like through an SEM?
- Does wetting recover? If so, how? How long does it take?
- What are the effects and consequences of a change in wetting? In particular how does it influence fluid flow and chemical transport including sorption? How does it affect colloid transport? How does it affect bacterial growth and migration? How does bacterial growth affect wetting?
- Can the consequences be mitigated? If so, how?

There is a role for the Environmental Engineer to play in addressing all of these issues, but the problem is multi-disciplinary. Various aspects of the problem require the expertise and services of surface chemists, material scientists, organic chemists, and microbiologists. Petroleum engineers and soil scientists can contribute. I also believe there is a role for mathematicians.

When two fluid phases and one solid phase contact, strange things can happen. The mathematics attempting to describe this behavior is classical. In the last year advances have been made with the techniques of cellular automata (CA) and molecular dynamics (MD). D. Rothman at MIT has produced the first two fluid phase automata models, using "red" and "blue" particles [Rothman, personal communication, 1988]. The particles interact on a grid using rules that satisfy the conservation laws of mass and momentum. By adding rules to describe the relative affinity of a "red" particle for another "red" particle, and similar rules for "blue" particles, Rothman has simulated interfacial tension. The solid surfaces are presently assumed to be neutral geometric boundaries, but this can change. By assigning "red" or "blue" properties to the walls various wetting conditions can be simulated, including the attachment of surface active colloids to the wall to represent wetting alteration. This would however require the intervention of "red-blue" surfactant particles. At Schlumberger-Dole three researchers - J. Koplick, J.R. Banavar, and J.F. Willemsen [1988] - have attacked the same problem using molecular dynamics [see also, *Physics Today,* 17-19, May, 1988]. Molecular dynamics represents "molecules," actually finite clumps of fluid molecules, and assigns a position coordinate and velocity vector to each "molecule." The "molecules" are allowed to interact, and the results are averaged out to obtain "fluid properties" such as fluid velocity. The Schlumberger group extended the MD approach to two fluids near a solid boundary. Where the fluid interface intersects the boundary, the classical no-slip condition vanishes. Curiously, they commented in *Physics Today* that CA could never handle the same two fluid phase problems. Two months later Rothman presented his CA results at a private research meeting. I guess the moral is that, in science, one should never be too sure of one's self. The difficulty with CA or MD is their need for copious super-computer time, preferably on a multi-processor machine like the hypercube Connection machine. In any event, these mathematical tools will make it easier to explore and understand some of the behavior we see in the lab and field.

How Does This Help?

There are three application areas that any rational research program in this field should contribute toward: monitoring and assessment; mitigation and remediation; and policy and regulation. Better understanding of wetting behavior and its influence will permit engineers to deal with each of these areas more effectively. During site investigations what do we look for, and where? What will happen if nothing is done? What is an effective remediation or treatment system, and how should it be operated? What policies or regulations are consistent with physical, chemical, and biological behavior? To illustrate, consider a typical pump and treat aquifer remediation scheme for an organic liquid. The ability of the system to "clean-up" the site will depend on the possible mobilization of the residual capillary-trapped organics, or the biotransformation of the organic to a more mobile or less threatening by-product. The efficacy of this system may be strongly influenced by wetting; but wetting has never been studied in this context. For some soils and some organics, it is possible that pump and treat systems will never be effective, and that wetting behavior may play a role in this lack of effectiveness. What should the policy be toward the encouragement, or discouragement, of pump and treat under these circumstances.

Can We Shorten the Time to Beneficial Use of Research?

The bottom line is that we need to determine whether or not wetting is an important issue. If we find that it is not, then we benefit by the realization that things are going to be easier than they might have been. If wetting is an important issue, we need to bring it to the attention of the user community, while we get to work on it. The problem has been left relatively unattended in environmental problems for so long, that I don't believe that the time for beneficial use can be shortened. There's a difference between scientific and engineering research. At this stage our scientific ignorance on the wetting problem makes it difficult to quickly develop engineering applications.

References

Adamson, A.W., *Physical Chemistry of Surfaces,* 4th Ed., Wiley, New York, 1982.

Albertson, M., G. Baldauf, F. Birk, Th. Dracos, A. Golwet, H. Horauf, W. Kab, P. Muntzer, G. Ruddiger, H.O. Schiegg, F. Schweisfurth, F. Schwille, H. Tangermann, H.G. Van Waegeningh, P. Werner, L. Zilliox, and L. Zwitting, "Evaluation and Treatment of Cases of Oil Damage with Regard to Groundwater Protection, Part 1, Scientific Fundamental Principles for Understanding the Behavior of Oil in the Ground," LTwS - Nr. 20, Federal Office of the Environment, West Germany, 1986. (English translation available from Battelle Pacific Northwest Laboratory.)

Amott, E., "Observations Relating to the Wettability of Porous Rock, *Trans., AIME, 216*, 156-62, 1959.

Anderson, W.G., "Wettability Literature Survey - Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability," *Journal of Petroleum Technology, 38*(10), 1125-44, Oct. 1986a.

Anderson, W.G., "Wettability Literature Survey - Part 2: Wettability Measurement," *Journal of Petroleum Technology, 38*(11), 1246-62, Nov. 1986b.

Anderson, W.G., "Wettability Literature Survey - Part 4: The Effects of Wettability on Capillary Pressure," *Journal of Petroleum Technology, 39*(10), 1283-1300, Nov., 1987a.

Anderson, W.G., "Wettability Literature Survey - Part 5: The Effects of Wettability on Relative Permeability," *Journal of Petroleum Technology, 39*(11), 1453-68, Nov., 1987b.

Anderson, W.G., "Wettability Literature Survey - Part 6: The Effects of Water Flooding," *Journal of Petroleum Technology, 39*(12), 1605-22, Nov., 1987c.

Baier, R.E., "Surface Properties Influencing Biological Adhesion," in R.S. Manly (Ed.), *Adhesion in Biological Systems*, Academic Press, New York, 15-48, 1970.

Baier, R.E., "Substrate Influence on Adhesion of Microorganisms and Their Resultant New Surface Properties," in G. Bitton and K.C. Marshall (Eds.), *Adsorption of Microorganisms to Surfaces*, Wiley, New York, 1979.

Bouchard, D.C., R.M. Powell and D.A. Clark, "Alkylammonium Cation Effects on Aquifer Material Sorptivity," *Agron. Abstr., 79*, 166, 1987.

Boyd, S.A., M.M. Mortland and C.T. Chiou, "Organo-clays as Sorbents for Organic Contaminants," *Agron. Abstr., 79*, 23, 1987.

Chatzis, I., N.R. Morrow and H.T. Lin, "Magnitude and Detailed Structure of Residual Oil Saturations," *SPE Jour., 23*(2), 311-325, 1983.

Corapcioglu, M.Y. and A.L. Baehr, "A Compositional Multiphase Model for Groundwater Contamination by Petroleum Products, 1. Theoretical Considerations," *Water Resourc. Res., 23*(1), 191-200, 1987a.

Corapcioglu, M.Y. and A.L. Baehr, "A Compositional Multiphase Model for Groundwater Contamination by Petroleum Products, 2. Numerical Solution," *Water Resourc. Res., 23*(1), 201-213, 1987b.

Corpe, W.A., "Attachment of Marine Bacteria to Solid Surfaces," in R.S. Manly (Ed.), *Adhesion in Biological Systems*, Academic Press, New York, 73-87, 1970.

De Bano, L.F. and J. Letey (Eds.), *Proceedings of Symposium on Water Repellent Soils*, Dept. of Soil Science and Agricultural Engineering, Univ. of California, Riverside, California, 354 pp., 1968

De Bano, L.F., J.F. Osborn, J.S. Krammes and J. Letey, "Soil Wettability and Wetting Agents...Our Current Knowledge of the Problem," *U.S. Forest Service Research Paper PSW-43*, Pacific Southwest Forest and Range Experiment Station, Berkeley, Calif., 1967.

Donaldson, E.C., R.F. Kendall, E.A. Pavelka and M.E. Crocker, "Equipment and Procedures for Fluid Flow and Wettability Tests of Geologic Materials," DOE/BETC/IC-79/5, Bartlesville Energy Tech Cntr., DOE, Bartlesville, OK, 1980.

Donaldson, E.C., R.D. Thomas and P.B. Lorenz, "Wettability Determination and Its Effect on Recovery Efficiency," *SPE Jour.*, 13-20, Mar., 1969.

Fried, A.N., "The Foam-Drive Process for Increasing Recovery of Oil," Rept. Inv. 5866, U.S. Bureau of Mines, Wash., DC, 1961.

Hornof, V. and N.R. Morrow, "Flow Visualization of the Effects of Interfacial Tension on Displacement," *SPE Reservoir Engineering*, *3*(1), 251-256, Feb. 1988.

Karnok, K.J., D.E. Radcliffe, K.A. Tucker, G.W. Landry, and R.W. Roncadori, "The Occurrence and Control of Hydrophobic Soil on Golf Course Putting Greens," Abstract, *EOS*, *68*(44), 1297, 1987.

Koplick, J., J.R. Banavar, and J.F. Willemsen, *Phys. Rev. Letr.*, *60*, 1282, 1988.

Krammes, J.S. and J. Osburn, "Water-Repellent Soils and Wetting Agents as Factors Influencing Erosion," in De Bano and Letey (Eds.), *Proc. Sym. on Water-Repellent Soils*, Dept. Soil Sci. and Agr. Engr., U.C. Riverside, 177-187, 1968.

Letey, J., J. Osborn, and R.E. Pelishek, "The Influence of the Water-Solid Contact Angle on Water Movement in Soil," *Bull. Int. Assoc. Sci. Hydrol.*, (3), 75-81, 1962.

Marsell, K.C. (Ed.), *Microbial Adhesion and Aggregation*, Springer-Verlag, KG, Berlin, 1985.

McPhee, J., "The Control of Nature, Los Angeles Against the Mountains-1," *New Yorker*, 45-78, September 26, 1988.

Melrose, J.C., "Interpretation of Mixed Wettability States in Reservoir Rocks," Paper SPE 10971, *SPE Fall Tech. Conf.*, New Orleans, 1982.

Miller, W.W., N. Valoras and J. Letey, "Movement of Two Nonionic Surfactants in Wettable and Water-Repellent Soils," *Soil Sci. Soc. Amer. Proc.*, *39*(1), 11-16, 1985.

Morrow, N.R., "Interplay of Capillary, Viscous and Buoyancy Forces in the Mobilization of Residual Oil," *Journ. Canadian Petro. Tech.*, *18*(13), 35-46, 1979.

Morrow, N.R., H.T. Lim, and J.S. Ward, "Effect of Crude-Oil-Induced Wettability Changes in Oil Recovery," *SPE Formation Evaluation*, *1*(1), 89-103, Feb., 1986.

Morrow, N.R., P.J. Cram and F.G. McCaffery, "Displacement Studies in Dolomite with Wettability Control by Octanoic Acid," *SPE Jour.*, Aug., 221-232, 1973.

Mortland, M.M., S. Shaobai and S.A. Boyd, "Clay-organic Complexes as Absorbents for Phenol and Chlorophenols," *Clays Clay Min.*, *34*(5), 581-585, 1986.

Nilsson, I. and M. Dostalek, "Estimation of the Biofilm Formation Ability of *Psedomonas putida* in Discrete Samples from Continuous Cultures," *Appl. Microbiol. Biotechnol.*, *20*, 182-188, 1984.

Pelishek, R.E., J. Osburn and J. Letey, "The Effect of Wetting Agents on Infiltration," *Soil. Sci. Soc. Amer. Proc.*, *26*, 595-598, 1962.

Pringle, J.H. and M. Fletcher, "Influence of Substratum Wettability on Attachment of Freshwater Bacteria to

Soil Surfaces," *Appl. Environ. Microbiol.*, *45*(3), 811-817, 1983.

Ransohoff, T.C. and C.J. Radke, "Mechanisms of Foam Generation in Glass-Based Packs," *SPE Reservoir Engineering*, *3*(2), 573-585, May, 1988.

Salathiel, R.A., "Oil Recovery by Surface Film Drainage in Mixed Wettability Rocks," *JPT*, 1216-1224, Oct. 1973.

Schiegg, H.O., "Fundamentals, Setups, and Results of Laboratory Experiments on Oil Propagation in Aquifers," VAX-Mitteilung No. 43, Versuchsanstalt fur Wasserbau, Hydrologie und Glaziologie, ZTH, Zurich, 1980. (English translation available from Battelle Pacific Northwest Laboratory.)

Schiegg, H.O. and J.F. McBride, "Laboratory Setup to Study Two-Dimensional Multiphase Flow in Porous Media," Proceedings of Conference on *Petroleum Hydrocarbons and Organic Chemicals in Ground Water*, Nat. Water Well. Assoc., Houston, 1987.

Schwille, F., "Migration of Organic Fluids Immiscible with Water in the Unsaturated Zone," in *Pollutants in Porous Media*, B. Yaron, G. Dagan and J. Goldsmid (Eds.), Springer-Verlag, Berlin, 1984.

Schwille, F., *Dense Chlorinated Solvents in Porous and Fractured Media. Model Experiments*, Lewis Publishers, Chelsea, Mich., 1988. (Translated by James F. Pankow.)

Taber, J.J., "Dynamic and Static Forces Required to Remove a Discontinuous Oil Phase from Porous Media Containing Both Oil and Water," *SPE Jour.*, 3-12, Mar. 1969.

Treiber, L.E., D.L. Archer and W.W. Owens, "A Laboratory Evaluation of the Wettability of Fifty Oil-Producing Reservoirs," *Society of Petroleum Engineers Journal*, (*SPEJ*), 531-540, Dec. 1972.

Treinen, R.J., W.E. Brigham and L.M. Castanier, "Apparent Viscosity Measurements of Surfactant Foam in Porous Media," SUPRI TR-48, Stanford Univ., Stanford, Calif., 1985.

Valoras, N. and J. Letey, "Quantitative Analysis for Nonionic Surfactants in Soil Leachates," *Soil Sci. Soc. Amer. Proc.*, *32*, 737-739, 1968.

Van Loosdrecht, M.C.M., J. Lyklema, W. Norde, G. Schraa, and A.J.B. Zehnder, "The Role of Bacterial Cell Wall Hydrophobicity in Adhesion," *Appl. Environ. Microbiol.*, *53*(8), 1893-1897, 1987a.

Van Loosdrecht, M.C.M., J. Lyklema, W. Norde, G. Schraa, and A.J.B. Zehnder, "Electrophoretic Mobility and Hydrophobicity as a Measure to Predict the Initial Steps of Bacterial Adhesion," *Appl. Environ. Microbiol.*, *53*(8), 1898-1901, 1987b.

Wang, F.H.L., "Effect of Wettability Alteration on Water/Oil Relative Permeability, Dispersion, and Flowable Saturation in Porous Media," *SPE Reservoir Engineering*, 3(2), 617-627, May, 1988.

Wardlaw, N.C., "The Effect of Pore Structure on Displacement Efficiency in Reservoir Rocks and in Glass Micromodels," Paper SPE 8843, *SPE/DOE Enhanced Oil Recovery Symposium*, Tulsa, April, 1980.

Wardlaw, N.C., "The Effects of Geometry, Wettability, Viscosity, and Buoyancy Forces in the Mobilization of Residual Oil," *Jour. Canadian Petro. Tech.*, *18*(3), 35-46, 1979.

Wilson, J.L., S.H. Conrad, E. Hagan, W.R. Mason and W. Peplinski, "The Pore Level Spatial Distribution and Saturation of Organic Liquids in Porous Media," Proceedings of Conference on *Petroleum Hydrocarbons and Organic Chemicals in Ground Water*, Nat. Water Well Assoc., Houston, Tex., 1988.

Wilson, J.L. and S.H. Conrad, "Is Physical Displacement of Residual Hydrocarbons a Realistic Possibility in Aquifer Restoration," Proceedings of Conference on *Petroleum Hydrocarbons and Organic Chemicals in Ground Water*, Nat. Water Well Assoc., Houston, Tex., 274-298, Nov., 1984.

Discussion: Physical Processes - Land

Linda M. Abriola
Environmental and Water Resources Program
Department of Civil Engineering
The University of Michigan
Ann Arbor, Michigan

It should be noted at the outset that this discussion was prepared without benefit of a preview of the speaker's paper. Hence this discussion is less a commentary or an elaboration of his major points. Rather it is a summary of my own view of research directions in the groundwater area and suggestions for ways to narrow the gap between the researcher and user communities.

My area of expertise is in the numerical modeling of fluid flow and contaminant transport in the subsurface. More specifically, my research work has focused on the development of mathematical models for the description of immiscible/miscible organic pollutant transport. Within this subject area, a number of important research directions can be identified. The first relates to the improvement of our understanding of immiscible organic phase entrapment in the saturated and unsaturated zones. Experimental and theoretical studies are needed to elucidate the mechanisms controlling this entrapment and to provide a concise mathematical description of this process for incorporation into multiphase flow models. Prediction of the configuration and persistence of an entrapped organic phase is of primary importance in the assessment of a contamination event and in the design of an effective remedial strategy. Another important research area is the study of interphase mass partitioning in multiphase fluid systems. The extent to which a nonaqueous phase organic liquid can volatilize or solubilize into the pore gas or water fluids will determine its migration potential. Sorption of the organic liquid or organic vapor onto the soil matrix could also be significant in this regard, but has received very limited attention. The efficiency of gas venting or soil flushing remediation schemes are closely tied to the above partitioning processes. The process of fingering also deserves closer scrutiny. Experimental evidence (1) suggests that, under certain circumstances, fingering may control the migration of nonaqueous phase liquids. The on-set of fingering and prediction of migration pathways, however, are not well understood. Existing mathematical models of the organic pollution process do not account for such flow instabilities. Finally, further work is needed on the development, validation, and calibration of numerical models designed to simulate multiphase contamination scenarios. Existing models are either extremely unwieldy, requiring numerous parameters and substantial computational effort for even small-scale problems, or are significantly over-simplified, neglecting important physical processes (2).

Taking a broader perspective for a moment, I believe that two central issues can be identified in relation to future directions in groundwater contamination research, which I shall term (a) integration and (b) scale. These same issues surfaced in a Forum on NSF Research Activities in Subsurface Systems held at the

University of Michigan in July 1986 (3) and have been commented upon in a number of recent review papers (4). Each is discussed briefly below.

By integration, I mean research which combines a number of disciplines and viewpoints to attack specific environmental problems. Even from the brief discussion above, it is clear that physical processes cannot be separated from the chemical, nor can modeling be separated from experimentation. Unfortunately, in this age of specialization, researchers tend to focus on relatively narrow research areas. Thus, it is clear that the complexity of environmental problems requires the collaboration of many investigators to achieve significant advances in the field. If whole aquifer clean-up is to be a major objective, it will require the expertise of hydrologists, soil scientists, chemists, microbiologists, systems analysts, etc. The trend toward collaborative work has already begun; a number of interdisciplinary conferences have been held (including the present AEEP meeting) and interdisciplinary journals are beginning to appear. I believe that this trend should continue. We, as educators, researchers, and administrators, should make every effort to breach the barriers which currently exist between disciplines and to encourage those who embark on collaborative endeavors.

The second broad issue which relates to future research directions is scale. There is an urgent need for controlled field experiments to validate laboratory-derived modeling approaches. Research must be directed towards the "scale-up" of theory and laboratory-measured parameters. Techniques for the measurement of meaningful field-scale parameters must be explored, as well as ways to incorporate uncertainty and heterogeneity into our modeling approaches.

It is generally acknowledged that field experiments are extremely costly. The quest for field "laboratories," thus, leads naturally to the promotion of university partnerships with government and/or industry. In addition to providing support for and access to field measurements, such partnerships can also serve to narrow the gap between users and researchers and help in the pooling of expertise. Research Centers established by the EPA and NSF in the last few years were conceived with this objective in mind. Through the participation on the advisory boards for these centers, industry may be kept apprised of the latest research developments. In this capacity, industry also has the opportunity to provide research direction to the university community. A study of the structure and success of these partnerships could help us develop a model for future industry-university relations.

It is my belief that we can also greatly reduce the gap between researchers and users through our role as educators of undergraduate engineers. We must instill in our students an appreciation for the complexities of environmental problems as well as the great benefits to be gained from inter-disciplinary cooperation. Students must learn that simplified approaches, although attractive, often give misleading or inappropriate results. They should be encouraged to read the scientific literature and to gain first-hand research experience where possible. By strengthening their ties to the research community, we may, thereby strengthen our ties to industry.

References.

1. Schwille, R., *Dense Chlorinated Solvents in Porous and Fractured Media, Model Experiments*, J.F. Pankow, trans., Lewis Publishers, Chelsea, Michigan, 1988.

2. Abriola, L.M., "Multiphase Flow and Transport Models for Organic Chemicals: A Review and Assessment," Electric Power Research Institute, EPRI EA-5976, September 1988.

3. Abriola, L.M. and W.J. Weber, Jr., "Summary Report, Forum on NSF Research Activities in Subsurface Systems," NTIS PB 88-102163, 1987.

4. U.S. National Report to International Union of Geodesy and Geophysics, 1983-1986, Contributions in Hydrology, *Reviews of Geophysics*, 25(2), 125-147, 1987.

Research Directions in Physical Processes - Water

Paul V. Roberts and Jeffrey R. Koseff
Department of Civil Engineering
Stanford University
Stanford, CA 94305-4020

Understanding physical processes is essential to understanding the state of environmental systems of all kinds, in natural waters and treatment operations alike. Physical processes affect the residence time and distribution of the constituents dissolved or suspended in water, as well as the interchange with other environmental compartments such as the atmosphere, lithosphere, and biosphere.

Scope

This paper offers an overview of fundamental research issues and directions related to the role of physical processes in natural waters and treatment operations. The need to consider the interrelationship among physical, chemical, and biological processes is pointed out, and a general philosophy is advanced that may help facilitate understanding and utilization of research results by the user community.

Interactions Among Processes

Physical processes are intimately coupled to chemical and biological processes to an extent that makes it difficult to segregate them according to the categories of this conference's program. For example, mixing, phase partitioning, and interphase mass transfer govern the local concentrations of contaminants; thus, these physical processes often constitute important controls on the rates of chemical and biological processes, and indeed often determine which reactions can proceed at significant rates. Indeed, some phenomena such as sorption can be driven by both physical and chemical mechanisms to a degree that renders the distinction futile. Moreover, the residence time of a constituent in a given portion of the environment, which is determined largely by physical processes, strongly influences the extent of reaction. As a further example, mixing and diffusion can mediate chemical conditions so as to exert a profound effect on chemical equilibria (Davidson, 1985). It is impossible to formulate a rational understanding of the behavior of environmental systems without accounting for such interactions among the various kinds of processes.

Scale and Variability

Central to the analysis of physical processes is an adequate grasp of fluid mechanics, particle dynamics, mass transport, energy transport, and phase equilibria. Basic understanding of all of these processes is adequate for analysis of simple problems, but difficulties invariably arise in applying the principles to real environmental systems because of their complexity, spatial heterogeneity, and temporal variability. The simple concept of the mass balance is a case in point: an accurate mass balance is requisite for a well-founded environmental problem analysis, and the methodology is straightforward. Yet it often proves extraordinarily difficult to implement an adequate mass balance in dealing with real environments, because it is infeasible to sample adequately over the relevant range of scales in time and space. Further, in real situations, the initial and boundary conditions frequently are insufficiently well known to permit reliable analysis and experimental design, not to speak of prediction.

Ideally, we should analyze environmental problems by developing understanding over the full range of scales of time and space relevant to the environmental system; this is clearly a formidable challenge, since the dimensions span some fifteen orders of magnitude, from the thousands of kilometers characteristic of some environmental compartments to the nanometer scale of molecular dimensions (National Research Council, 1988). Similarly, the relevant time scales cover some twelve orders of magnitude, from the millisecond range for fast reactions and turbulent eddy transport to the thousand year timeframe for long-term waste disposal and groundwater movement.

Physical Processes in Natural Waters

In our treatment of this section we adopt the posture that the basis for rational decisions should be the predictive capability of accurate three-dimensional simulation models which realistically capture not only all the relevant hydrodynamic influences, but also represent the interaction between the hydrodynamics, the chemistry, and the biology. This is not to say that the major focus of the research should be on the development of the models *per se*. A growing body of computational fluid dynamicists have already begun to address the hydrodynamic and numerical problems associated with building accurate, realistic models for environmental flows such as lakes, reservoirs, estuaries, and streams. However, the focus should be on developing a more complete understanding of the physical, chemical, and biological processes in these flows, **particularly** with respect to the interaction between these processes.

Sheng (see Gray, 1986) has stated that "To be an effective long-term simulator of a variety of flow situations, an ideal numerical model should be comprehensive (containing the proper physics) and generalized (requiring minimal tuning, and adaptable to various applications) in terms of its dynamic features, while accurate (containing little numerical damping and dispersion) and economical (computationally efficient) in terms of its numerical features".

As we stated above, the vast majority of lakes, reservoirs and other naturally occurring surface waters are heterogeneous, both temporally and spatially. Indeed, as Ferrara (see Gray, 1986) states "No lake is ever static. Several time frames are of significance. Diurnal... Seasonal... Geologic...". For example, the baroclinic motions associated with internal density variations occur on time scales much longer than surface wave barotropic motions. In addition, plunging inflows and sidearms respond on a different time scale to the whole water body, yet the interaction between the sub-domain and the whole is strong (see Fischer and Smith, 1983). The transport and mixing of pollutants is also affected by variation in length scales. As Blumberg (see Gray, 1986) notes, "Mixing is accomplished by a hierarchy of processes with different length scales...wind-driven gyres (100km) to intermediate eddies (10km) to molecular viscosity and diffusion."

Because of the large disparity in the size of the scales it is often the case that the smaller scale motions remain unresolved in simulation modeling. Yet, as Blumberg states, "Unresolved turbulent motions can result in significant transports of momentum, heat, nutrients, and pollutants. They also interact dynamically with the larger scale eddies explicitly resolved in the model and progressively degrade the accuracy of the model predictions".

In this paper, then, we would like to focus more on this very problem, which is one of the major shortcomings in our present modeling approach. We would like to preface our remarks by acknowledging that traditional turbulence models for the unresolved time or spatial motions have been successful to a degree in the past (Sheng in Gray 1986) and indeed have a useful role. However, recent efforts in modeling flows in natural water bodies have met with limited success. Rodi (1987) provides a fairly comprehensive review of the state-of-the-art in modeling stratified flows. From this review it has become apparent that meaningful engineering calculations which represent all the relevant processes occurring in environmental flows cannot be achieved with our present modeling approach or with the turbulence models presently used for treating unresolved scales of motion.

It is quite obvious, therefore, that given the demands of a successful simulation, the realities of the size and physics of lakes and reservoirs, and the constraints imposed by present computer technology and our budgets, a new modeling approach is needed. Dividing the problem into smaller, more tractable sub-domains based on bathymetry, physics, chemistry, and biology, and using boundary conforming coordinate systems, are two methods presently being investigated to counter the problems described above in a realistic manner (Meakin, 1986, and Perng and Street, 1987). Furthermore, the use of adaptive gridding offers a very promising solution to the problem of sufficient grid resolution (Skamarock et al., 1989).

The problem, however, goes beyond the numerical fixes described above. One of the major problems with the traditional second-order closure (turbulence) models presently used in our simulation schemes is that these models cannot faithfully represent the unresolved scales that lie between the "true" turbulent scales and the lower limit of the grid used in the numerical calculations. In most cases the "true" turbulence is often confined to scales well below those resolved by the numerical models. Thus the major issue should be the construction of models of unresolved motions, whether they are turbulent or not, and **NOT** the construction of "turbulence models".

Our major effort should, therefore, be on constructing and verifying proper parameterizations for the unresolved motions. These parameterizations could then be used in conjunction with eddy-resolving numerical codes (Large Eddy Simulation). The effect of all the length scales not resolved by the grid itself would then be captured by the parameterization model. This strategy involves a number of important steps, including identifying the important physical processes present in the relevant environmental flows, and developing a basic understanding of these processes.

What then are the relevant environmental flows that should be used for developing the parameterizations? For purposes of this discussion, let us consider the relevant surface water flows to be those in lakes, reservoirs, estuaries, and streams. In order to understand these flow systems it is necessary to identify all the factors influencing the advective or transportive process, the mixing and dispersion processes, and the processes influencing the interaction of the flow with the atmosphere as well as the benthos and sediments. The following are examples that are most relevant to the task of parameterizing unresolved scale motions.

1. The surface stress at an air-water interface due to the wind is an extremely important factor in the transport of heat, mass, and momentum through this interface. Significant work has been done on the problem of rearation, and momentum and heat transfer at the air-water interface. Additional work is now necessary into understanding the transport of pollutants through the water column and into the atmosphere. In addition, understanding of the interfacial exchange process is essential to coupling the atmosphere to the water column. The problem of acid rain and its influence on the health of natural water bodies comes to mind in this respect.

2. The vast literature on turbulent boundary layers needs to be marshalled in order to understand the interaction between the benthos and the overlying water column. Whereas mass transfer processes at the boundaries in internal and aerodynamic flows are fairly well understood, they are not that well understood at natural interfaces. For example, an emerging body of (largely circumstantial) evidence suggests that benthic suspension feeders may be important in mediating the flux of particulates and their adsorbed species (nutrients, contaminants) from the water column to the sediments and thereby act as a natural control on eutrophication. (Cloern, 1982). This issue cannot be addressed rigorously, however, until we understand the mechanisms and rates of particle ingestion by benthic filter feeders. This means we need to understand not only the influence of the near-bed hydrodynamics on the flux of suspended particles from the water column to the benthos, but also the possible effect of filter feeders (bivalve mollusks), for example, on the flow properties near the bed.

3. Advection of pollutants in estuaries. There is a complex interaction between the bathymetry, the Coriolis force, the tides and fresh water inflows which is not completely understood. The work by Huzzey and Brubaker (1988) on the York River Estuary is a good example of this.

4. Inflows to estuaries, lakes and reservoirs. The behavior of the fresh water/salt water interface in a partially mixed or salt-wedge type estuary will determine the transport of pollutants to/from the estuary and thereby the dilution capacity of the estuary. The recent study by Denton and Hunt (1986) is a good example of this. The stream inflow to lakes and reservoirs is extremely important as well in this regard. Mixing in the inflow zone will determine at what level the incoming waters are inserted into the reservoir and thereby where the nutrients, sediments, and contaminants are likely to be inserted. At present no rigorous solution is available for plunging inflows. In particular, the relationship between the mixing processes occurring within the plunge and the relevant parameters describing the flow regime are not well defined.

5. Turbulence in stratified systems. Much of the mixing and dispersion in natural systems is due to shear induced turbulence. However, the turbulence is modified by the rotation and buoyancy forces which are present in these systems. Any attempt to model mixing and dispersion of pollutants in stratified systems depends on our ability to characterize the behavior of the turbulence in the presence of stratification, which is very limited. Research to date has raised more questions than supplied answers (van Atta, 1985, and Hopfinger, 1985).

Physical Treatment Operations

For the most part, physical treatment operations in environmental engineering applications are founded on well established principles of chemical and mechanical engineering, adapted to the exigencies of water treatment and pollution control situations (Metcalf and Eddy, 1979; Montgomery, 1985; Weber, 1972). The unit operations approach combining mass balances, mixing models, equilibrium relations, and rate expressions has proven widely successful, especially where substantial empirical data are available for calibrating methods and models. Even complex mixtures of contaminants have been dealt with adequately by lumping together groups of contaminants that behave similarly into collective parameters.

Individual Contaminant Limitations

Nonetheless, the unit operations approach as employed traditionally in environmental engineering has severe limitations when it comes to considering explicitly a broad pallet of individual contaminants, including their interactions. The pervasive regulatory trend toward formulating specific limitations for a multitude of individual contaminants presents a new set of challenges for designers of treatment operations, and hence for researchers who aim to provide a sound basis for process selection and analysis. We need to improve conceptual and mathematical models for assessing the effectiveness of alternative process alternatives for treating individual contaminants and their mixtures, and for estimating equilibrium and rate parameters to be used as inputs in those evaluations.

If the individual contaminants can be considered separately, without accounting for competition or similar interactions, the tasks of process analysis, selection, and design are greatly simplified. However, if substantial interactions must be accounted for in dealing with contaminant mixtures, those tasks are impeded severely. The seemingly simple matter of deciding when interactions among contaminants can be safely neglected, and when they must be taken into account, leads us into largely uncharted territory in which the most experienced researchers and practitioners risk losing their bearings. The criteria differ among treatment operations, depending on the physical principle of separation and the nature of the contaminants and their potential interactions.

Predicting the equilibria and rates of physical processes and the values of associated properties is a well-developed art (Lyman et al., 1982), compared to the analogous task of predicting chemical reaction rates. Accordingly, the difficulties of predicting interactions among contaminants are less severe where physical processes predominate than where chemical phenomena play a major role. Seemingly, there are important differences also between steady-state and non-steady-state treatment processes, with nonsteady-state situations presenting special difficulties if observed over a wide range of time scales.

Hydrophobic partitioning is an example of a physical phenomenon that has proven remarkably amenable to generalized prediction even in complex environmental systems. Hydrophobic partitioning concepts have been applied to aqueous solubility as well as to partitioning into organic liquids, lipids, sediments, soils, aquifer solids, and air (Chiou, 1985; Karickhoff et al. 1979; Karickhoff, 1984; Leighton and Calo, 1981; Means et al., 1982; Schwarzenbach and Westall, 1981). Where the phase partitioning is governed by the hydrophobic effect, it is possible to predict the distribution of a chemical between aqueous solution and other phases based on the aqueous activity coefficient, which can be estimated using a group contribution method such as UNIFAC if data are lacking (Arbuckle, 1986; Campbell and Luthy, 1985; Gmehling et al; 1982; Munz and Roberts, 1987). These approaches also can be applied to well-defined mixtures to assess concentration effects (Munz and Roberts, 1986). Generalized approaches to environmental modeling that incorporate the fugacity concept to quantify partitioning among environmental compartments (Mackay, 1979) show great promise as a tool for analyzing the transport, distribution, and persistence of chemicals in the environment.

However, simple partitioning approaches usually fail to account properly for specific interactions between solute and sorbing solid (Westall, 1987), and are inadequate for dealing with ionic organic compounds and inorganic compounds. Adsorption onto granular activated carbon, the most widely used adsorbent in water and wastewater treatment, is characterized by strong competition among solutes. Quantitative models are available for predicting competition among well-defined solutes (Crittenden et al., 1985; DiGiano et al., 1978; Radke and Prausnitz, 1972), but serious anomalies arise when substantial quantities of natural organic matter are present, reducing the adsorption capacity for compounds of low molecular weight. This competition is time-dependent and appears to reflect preloading with natural organic matter that is subsequently difficult to displace (Baldauf, 1986; Zimmer et al, 1987). Because fixed bed adsorption is a semi-continuous process in which solute concentration fronts move at different rates through the adsorber bed, the wave of natural organic matter permeates faster into the depth of the bed, and once adsorbed is difficult to displace (Summers and Roberts, 1987). It is not yet clear whether interactions of this sort are caused by physical or chemical mechanisms, although adsorption of organic solutes by activated carbon is thought to be governed mainly by physical forces. Whatever the cause, accounting properly for this kind of competition seriously complicates the task of designing adsorbers for water and wastewater treatment.

Facilitating Interactions Between Researchers and the User Communities

Understanding environmental processes is a worthy end in itself, and those conducting fundamental research need the freedom to conduct their work without being overly encumbered by attachment to case-specific problems. Nonetheless, the research effort must be justified in terms of its utility in defining and solving problems. Researchers play a variety of roles that enrich user communities, including decision makers and other government officials, organizations active in water supply and water pollution control, and consultants. To be useful, the research insights must be translated into terms that are understandable to the users, who also must be convinced that the research results are relevant to their problems.

To enhance this interaction and acceptance, it is advantageous for researchers and users to work together directly in formulating practical, scientifically founded approaches in setting policy, analyzing problems, and developing technical solutions. One way of effecting this collaboration is through research that focuses on fundamental processes in a natural setting. By focusing on problems in real environments, researchers can assure that they emphasize real problems, and that they identify the processes that are relevant to the environment. Moreover, they increase their chance of recognizing the important interactions among different processes, and of identifying processes that predominate at large scales of time and distance. The analog with respect to treatment processes entails systematic investigation of treatment operations at full scale over extended periods under the influence of representative, varying conditions.

Whether dealing with natural environments or treatment applications, the most convincing demonstrations of adequate conceptual understanding are those that entail interpreting and predicting a system's transient behavior under the influence of strong forcing. For example, a major chemical or oil spill like that which recently occurred in the Ohio River system in recent years presents a unique opportunity to test and improve understanding of physical transport processes in streams. However, there usually are practical constraints to creating such forcing conditions, especially in natural environments. We should take advantage of those opportunities that do arise, by establishing a mechanism to mobilize and support research on environmental processes in real systems following catastrophic perturbations.

Investigations of real, large-scale systems usually are more applied than fundamental, and the results tend to be case-specific and empirical. But, if conducted thoughtfully and with a view toward process analysis, such investigations can provide insights that transcend the particular situation being studied. Indeed, this approach is most effective if large-scale studies are coordinated with controlled experimentation to identify and characterize process mechanisms with well-defined systems at the laboratory scale.

Appropriate mathematical model development plays a crucial role in expressing process understanding in operational form, facilitating the design and interpretation of experiments, estimating parameter values from experimental data, and generalizing the results of the research. A schematic of the integrated approach combining these diverse research activities is shown in Figure 1. This integrated research strategy is inherently suited for improving understanding of chemical and biological processes as well as physical ones, and also their interactions, and in fact becomes more crucial the greater the complexity of the situation under study. To achieve complete understanding of complex environmental problems, only a holistic approach will suffice.

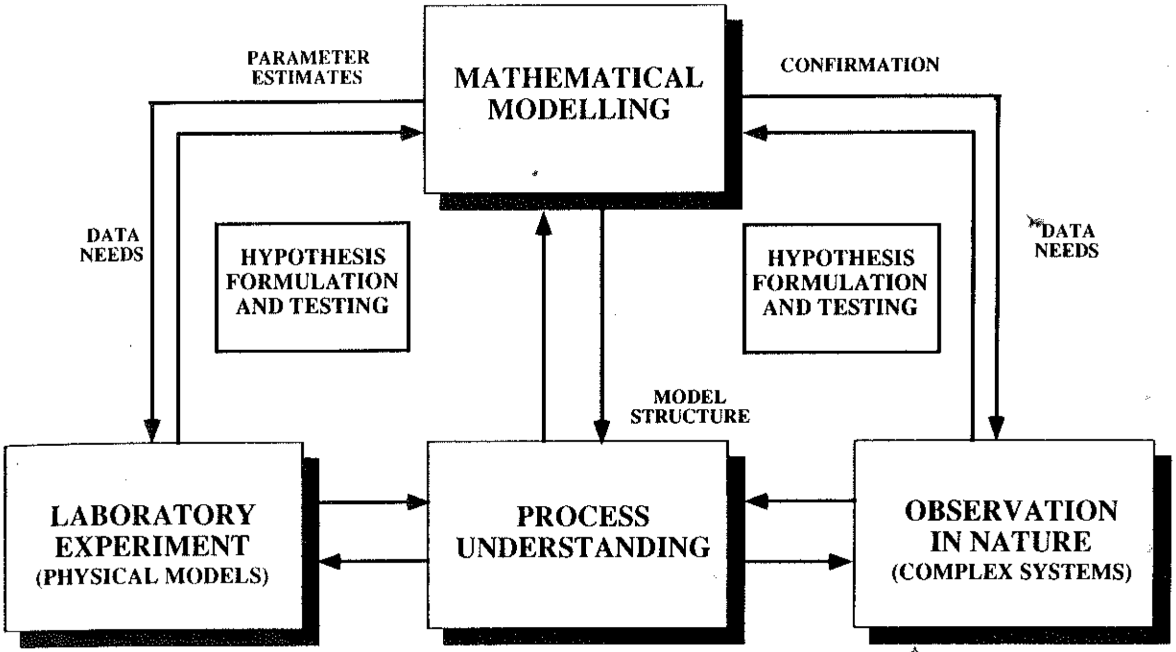

Figure 1: Schematic showing interrelations among hypothesis, experiment and modelling.

References.

Arbuckle, W.B., 1986. "Using UNIFAC to Calculate Aqueous Solubilities", Environ. Sci. Technol., 20(10), 1060-1064.

Baldauf, G., "Influence of Natural Organic Substances on the Adsorption of Synthetic Organics in GAC-Filters", Vom Wasser, 67, 11-21.

Campbell, J.R., and R.G. Luthy, 1985. "Prediction of Aromatic Solute Partition Coefficients Using the UNIFAC Group Contribution Model," Environ. Sci. Technol., 19(10), 980-985.

Cloern, J.E., 1982. "Does the Benthos Control the Phytoplankton Biomass in South San Francisco Bay?," Mar. Ecol. Prog. Ser., 9, 191-202.

Chiou, C.T., 1985, "Partition Coefficients of Organic Compounds in Lipid-Water Systems and Correlations with Fish Bioconcentration Factors," Environ. Sci. Technol., 19(1), 57-62.

Crittenden, J.C., P. Luft, D.W. Hand, J.L. Oravitz, S.W. Loper, and M. Ari, 1985. "Prediction of Multicomponent Adsorption Equilibria Using Ideal Adsorbed Solution Theory," Environ. Sci. Technol., 19(11), 1037-1043.

Davidson, W., 1985. Conceptual Models for Transport at a Redox Boundary, pp. 31-53 in Chemical Processes in Lakes, W. Stumm, ed., Wiley-Interscience.

Denton, R.A., and J.R. Hunt, 1986, "Currents in San Francisco Bay - Final Reports," UCB/HEL-86/01, Hydraulic and Coastal Engineering, University of California, Berkeley, CA.

DiGiano, F.A., G. Baldauf, B. Frick, and H. Sontheimer, 1978. "A Simplified Competitive Equilibrium Adsorption Model", Chem. Eng. Sci., 33, 1667-1673.

Fischer, H.B., and R.D. Smith, 1983. "Observations of transport to surface waters from a plunging inflow to Lake Mead," Limnol. Oceanog., 28(2), 258-272.

Gmehling, J., P. Rasmussen, and A. Fredenslund, 1982. "Vapor-Liquid Equilibria by UNIFAC Group

Contribution, Revision and Extension, 2", Ind. Eng. Chem. Proc. Des. Dev., 21, 118-127.

Gray, W.G., (Ed.), 1986. Physics-based modeling of lakes, reservoirs and impoundments, ASCE, New York.

Hopfinger, E.J., 1985. "Turbulent Collapse in Stratified Fluids, Proc. IUTAM Symp. on Mixing in Stratified Fluids, Margaret River, Australia.

Huzzey, L.M., and J.M. Brubaker, 1988. "The formation of longitudinal fronts in a coastal plane estuary," Journal of Geophysical Research, 93, 1329-1334.

Imboden, D.M., and R.P. Schwarzenbach, 1985. Spatial and Temporal Distribution of Chemical Substances in Lakes: Modeling Concepts, pp. 1-30 in Chemical Processes in Lakes, W. Stumm, ed., Wiley Interscience.

Karickhoff, S.W., D.W. Brown, and T.A. Scott, 1979. "Sorption of Hydrophobic Pollutants on Natural Sediments," Water Research, 13, 241-248.

Karickhoff, S.W., 1984. "Organic Pollutant Sorption in Aquatic Systems," J. Hydraulic Eng., 110, 707-735.

Leighton, D.T., Jr., and J.M. Calo, 1981. "Distribution Coefficients of Chlorinated Hydrocarbons in Dilute Air-Water Systems," J. Chem. Eng. Data, 26(4), 382-385.

Lyman, W.J., W.F. Reehl, and D.H. Rosemblatt, 1982. Handbook of Chemical Property Estimation Methods, McGraw-Hill Book Co., New York.

Mackay, D., 1979. "Finding Fugacity Feasible", Environ. Sci. Technol., 13(10), 1218-1223.

Meakin, R.L., 1986. "Application of boundary conforming coordinate systems and domain decomposition principles to environmental flows," Ph.D. Dissertation, Dept. of Civil Engineering, Stanford University, Stanford, CA 94305-4020.

Means, J.C., S.G. Wood, J.J. Hassett, and W.L. Banwart, 1982, "Sorption of Amino- and Carboxy-Substituted Polynuclear Aromatic Hydrocarbons by Sediments and Soils," Environ. Sci. Technol., 16(2), 93-98.

Metcalf and Eddy Inc., 1979. Wastewater Engineering Treatment, Disposal, Reuse, 2nd Edition, McGraw-Hill, New York.

Montgomery Consulting Engineers, Inc., 1985. Water Treatment Principles and Design, Wiley-Interscience.

Munz, C., and P.V. Roberts, 1986. "Effects of Solute Concentration and Cosolvents on the Aqueous Activity Coefficient of Halogenated Hydrocarbons," Environ. Sci. Technol., 20(8), 830-836.

Munz, C., and P.V. Roberts, 1987. "Air-Water Phase Equilibria of Volatile Organic Solutes," J. Amer. Water Works Assoc., 79(5), 62-69.

National Research Council, 1988. Frontiers in Chemical Engineering - Research Needs and Opportunities, N.R. Amundson et al., eds., National Academy Press, Washington, D.C.

Perng, C-Y., and R.L. Street, 1987. "Improved numerical codes for solving three-dimensional and unsteady flows," Fifth Int'l. Conf. Numer. Meth. Lam. and Turb. Flows, 1, 12-22.

Radke, C.J., and J.M. Prausnitz, 1972. "Thermodynamics of Multi-Solute Adsorption from Dilute Liquid Solutions," AIChE Journal, 18(4), 761-768.

Rodi, W., 1987. "Examples of calculation methods for flow and mixing in stratified fluids," J. Geophysical Research, 92, C5, 5305-5328.

Schwarzenbach, R.P., and J.C. Westall, 1981. "Transport of Nonpolar Organic Compounds from Surface Water to Groundwater, Laboratory Sorption Studies," Environ. Sci. Technol., 15, 1360-1367.

Summers, R.S., and P.V. Roberts, 1987. "Activated Carbon Adsorption of Humic Substances, I., Heterodisperse Mixtures and Desorption," J. Coll. Interface Sci., 122 (2), 367-381.

Skamarock, W., J. Oliger, and R.L. Street, 1987. "Adaptive grid-refinement for numerical weather prediction," J. Computational Physics, 80 (1), 27-60.

van Atta, C.W., 1985. "Some Challenges for Modeling of Turbulence and Internal Waves in Stably Stratified Fluids," in Macroscopic Modeling of Turbulent Flow and Fluid Mixtures, O. Pironneau, ed., Springer.

Weber, W.J., Jr., 1972. Physico-Chemical Processes for Water Quality Control, Wiley-Interscience.

Westall, J.C., 1987. "Adsorption Mechanisms in Aquatic Surface Chemistry", in Aquatic Surface Chemistry, W. Stumm, ed., Wiley Interscience, pp. 3-32.

Zimmer, G., and H. Sontheimer, 1987. "Activated Carbon Adsorption of Organics in the Presence of Humic Substances", American Chemical Society Division of Environmental Chemistry, Preprints of 123rd National Meeting, Denver, CO, Vol. 27, No. 1, pp. 346-348.

Discussion: Physical Processes - Water

Desmond F. Lawler
Department of Civil Engineering
University of Texas
Austin, TX 78712

Research Directions and Approach

Roberts and Koseff have presented a novel approach to research, one that is likely to achieve the desired goals of increasing interactions between researchers and users and shortening the time gap between research advances and their application in environmental engineering situations. Their idea is similar to, but a significant advance on, a research methodology that I have espoused. That methodology is summarized in Figure 1; in scientific or engineering research, a question can be addressed either mathematically or experimentally. The question can be translated into a mathematical formulation and the resulting solution constitutes an answer to the original question; this concept was taken from the preface to Kreyszig's book on *Advanced Engineering Mathematics* (1972). Alternatively or additionally, the question can be translated into an experimental investigation and the experimental results also constitute an answer to the question. The advantage of taking both approaches is that one can compare the results. If they agree with one another, one can be confident of one's understanding and probably apply the results in a wide variety of applications. If they disagree, the process is likely to identify the weak points in our understanding and thereby enable us to improve that understanding (and perhaps design our next piece of research).

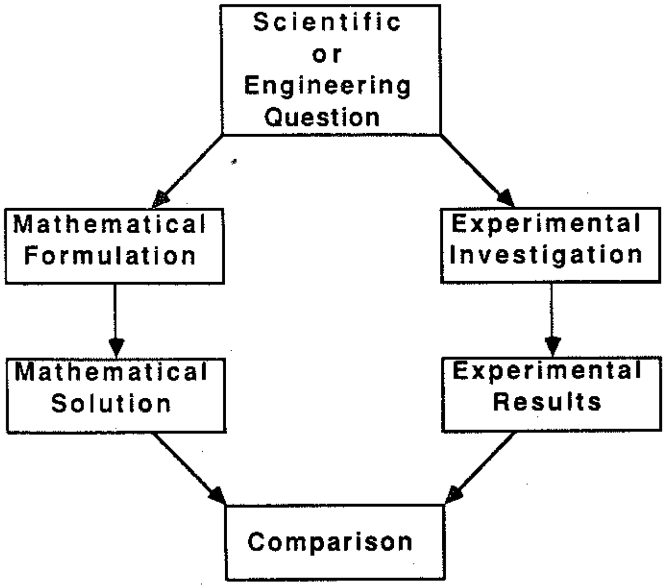

Figure 1: Generalized Research Approach

The advance that Roberts and Koseff have included is the incorporation of the distinction between simple and complex systems. Taking some liberty, I have taken their ideas and put them into my type of diagram as shown in Figure 2. If this diagram is an adequate translation of their ideas, their addition is obvious--a third branch representing the complex, full-scale, or field system and measurements within that system to compare with both the simple system experimental results and the mathematical solution. The addition is an important one, because it allows a check on whether the translation of the original question into the mathematics or the laboratory-scale experimental investigation incorporated all the essential features of the complex system. The challenge facing investigators in our field is to incorporate all three approaches--too often, investigators have followed only one of these three paths and it is too easy to misinterpret one's results without the internal check of the other research strategies. In particular, I believe that the mathematical approach has been overlooked too often in our field, retarding the generalization and widespread use of new understanding.

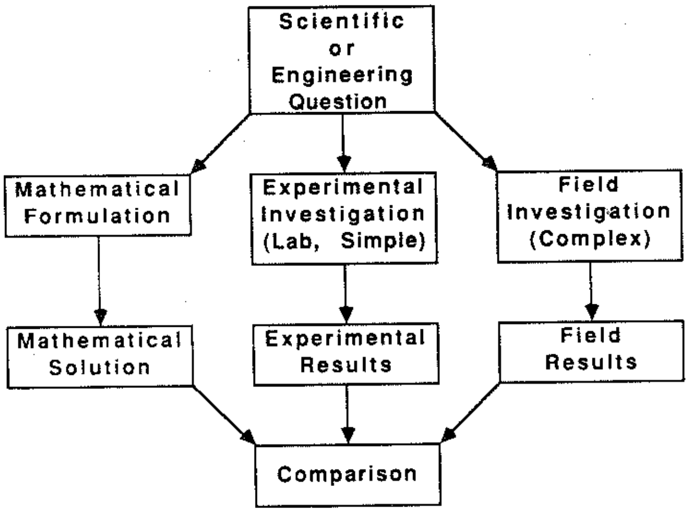

Figure 2: Generalized Research Approach, Modified to Incorporate Concepts of Roberts and Koseff

A second idea in the Roberts and Koseff paper that deserves more attention and expansion is the relationship between the microscopic and macroscopic. Engineers are concerned with macroscopic systems; within our purview, these systems are natural water bodies or treatment processes and systems. Nevertheless, we have reached the end of the road, in my opinion, in trying to make progress by only studying phenomena on the macroscopic level. The age of TOC, BOD, or solids concentration is over; now we must study individual compounds or groups of compounds or particle size distributions to progress. While we must be more concerned with the microscopic phenomena, studying at the microscopic level alone is equally insufficient. The relationship between the microscopic and macroscopic, between the research and application, between the science and technology, must always be kept in mind if our research results are to be useful. Examples are given below.

Physical Processes--Water

Roberts and Koseff have properly pointed out that many environmental situations do not confine themselves to the limitations of a single element in the conference matrix, but several phenomena or processes in water are primarily physical in nature. Chief among these are transport and separations. The issues of transport were nicely summarized by Roberts and Koseff; in short, these issues need a lot of research, especially in those situations where the relevant scales of transport span several orders of magnitude. Just recently, a student concerned with dispersive transport and reactions in estuaries asked me if it would be possible to model both processes simultaneously with a random walk approach. It did not take long to realize that, while transport and reactions can *each* be studied with this approach, the length scales are so different that it is at least impractical to put both together in the same problem.

Separations are primarily physical processes, and are important both in natural and engineered environmental systems; major examples include sedimentation, sorption, gas transfer processes, and membrane separations.

Sedimentation presents an interesting illustration of the role of research in physical processes. First, it is of critical importance in both natural waters (where it determines the fate of many constituents, not just the particles themselves) and engineered treatment systems (where it is by far the most common separation process). Second, as a process with a long history, we think we know a lot about it, and yet several questions remain unanswered. The state of our knowledge can be illustrated with the diagram in Figure 3, with the three axes showing the variables which influence sedimentation behavior: particle concentration, flocculent characteristics, and heterogeneity. The simplest case (point A in the diagram) is that of the single particle; Stokes solved this problem over 100 years ago. The amazing fact is that Point A is the only point on the diagram which we can claim to understand fully, although we routinely design engineered systems for the opposite pole. Point B represents the case of thickening of suspensions which are concentrated, heterodisperse, and flocculent, i.e., all sludges of interest in our treatment plants and probably the top layers of sediment in natural waters. We design sludge thickening facilities that work, but they are costly and cause operational headaches. Point C represents the flocculent suspensions such as those in settling tanks in treatment plants or the particles in lakes. We cannot yet claim to be able to predict the behavior of such suspensions, even if we know fully the chemistry, size distribution, and flow patterns of the situation. To improve the design of engineered systems for either type of suspension, we need to know more about the microscopic behavior of particles. Progress is being made on understanding two particle interactions (e.g., Jeffrey and Onishi, 1984) and on behavior of suspensions (Russel, 1987); my view is that such progress with the microscopic approach is the most promising (and only?) approach leading to better understanding and ultimately better designs for the macroscopic cases of interest.

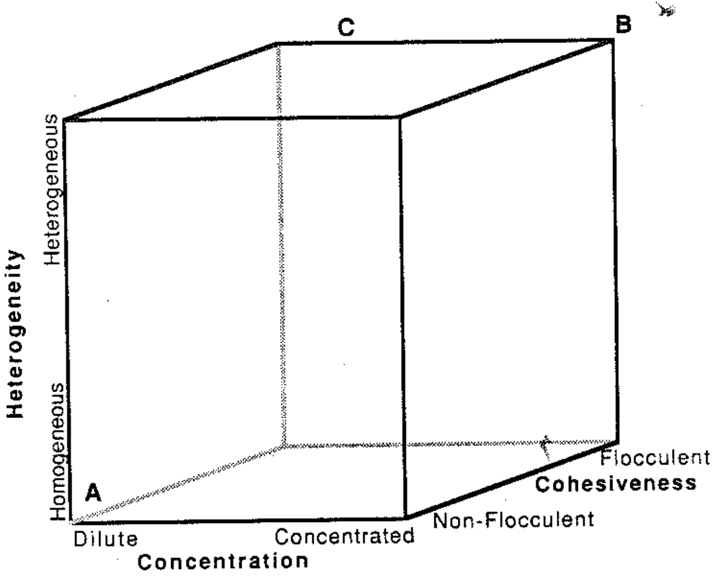

Figure 3: Three dimensional sedimentation paragenesis diagram.

Roberts and Koseff noted the significant progress made in recent years in understanding multi-component systems, sorption in particular. Progress in understanding gas transfer processes, their relevance and applicability to environmental systems has also been great. Roberts and several co-workers (Roberts and Levy, 1985; Roberts et al., 1985; and Munz and Roberts, 1987) have been key players in this regard. Here the progress has stemmed from learning what was known in other fields (in this case, chemical engineering) and applying it to environmental situations; the differences were primarily issues of concentration (much lower in most environmental engineering applications than in chemical engineering applications) and mixtures (often more heterogeneous in environmental engineering applications). To be sure, more can yet be learned for both these types of separations, but the mathematical models show excellent agreement with both laboratory scale experiments and field scale measurements.

An area with a large future but little history in the field of environmental separations is that of membrane processes. The field is developing rapidly, with increasing applications in several industries and the creation of new and better membranes monthly. The applications in the water industry are also growing; membrane processes are routinely used in making high purity water for manufacturing processes such as for circuit boards and for the food industry. Membrane processes have potentially wide use in drinking water treatment in the near term and perhaps ultimately in wastewater treatment. This area represents a challenge to environmental engineering research; we are, as a profession, behind the times and need to learn and expand the knowledge in this area to make it a more viable and common process.

Conclusions

These are interesting times to be involved in research on physical processes in water; we are, it seems, both knowledgeable and ignorant. Questions abound, and need answering. Progress in answering these questions lies in two interrelated approaches. First, our research, on physical processes in water (at least), should combine mathematical modeling, laboratory investigations, and field investigations. Second, we must study microscopic (time and space) phenomena and, simultaneously, their relationship to macroscopic phenomena to increase our understanding and improve technology at the macroscopic level.

References.

Jeffrey, D.J., and Onishi, Y., "Calculation of the Resistance and Mobility Functions for Two Unequal Spheres in Low Reynolds Number Flow", J. Fluid Mechanics, 139, 261-290, 1984.

Kreyszig, E., *Advanced Engineering Mathematics*, (Third Edition), Wiley, New York, 1972.

Munz, C., and Roberts, P.V., "Air-Water Phase Equilibria of Volatile Organic Solutes", Journal of the American Water Works Association, 79, 5, 62-69, 1987.

Roberts, P.V., Hopkins, G.D., Munz, C., and Riojas, A.H., "Evaluating Two-Resistance Models for Air Stripping of Volatile Organic Contaminants in a Countercurrent, Packed Column", Environmental Science and Technology, 19, 164-173, 1985.

Roberts, P.V., and Koseff, J.R., "Research Directions in Physical Processes--Water", Proceedings of the AEEP Conference on Fundamental Research Directions in Environmental Engineering, Washington, D.C., 1988.

Roberts, P.V., and Levy, J.A., "Energy Requirements for Air Stripping Trihalomethanes", Journal of the American Water Works Association, 77, 4, 138-146, 1985.

Russel, W.B., *The Dynamics of Colloidal Systems*, University of Wisconsin Press, Madison, 1987.

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Conversations with Gerald W. Culkin and Mooyoung Han, Doctoral candidates at the University of Texas, were helpful in formulating the ideas in this paper.

Summary Discussion - Physical Processes

John H. Seinfeld
Department of Chemical Engineering
California Institute of Technology
Pasadena, California

It was noted in the discussion period that the subject of process technology in air pollution emissions control had not been addressed in the two air papers. A discussion of the adequacy of atmospheric emissions inventories ensued. It was noted that the historical perception has been that mobile source inventories, especially for hydrocarbons, are considerably more accurate than those for stationary sources. Recent data indicating that evaporative hydrocarbon emissions from motor vehicles may be substantially greater than previously thought have called into question our perception of the accuracy of mobile versus stationary source emissions inventories. The lack of a national program of ambient hydrocarbon monitoring has made it very difficult to assess if hydrocarbon emissions reductions have, in fact, occurred as estimated. Rather, urban ozone levels have been used as a surrogate to assess the success of hydrocarbon controls rather than direct hydrocarbon measurements, and the fact that ozone levels have not decreased as much as expected suggests that hydrocarbon emissions may have been underestimated. Such underestimates will lead to underprediction of ozone and associated pollutants in air pollution models.

The subject of indoor air pollution was also not addressed in the two presentations. It was noted that the calculation of indoor exposure poses a substantial problem. Physical processes unique to the indoor environment include deposition of pollutants on indoor surfaces. These processes are poorly understood at present.

The physical processes-land papers focused on problems of multiphase flow in porous media. As in the air area, the importance of mathematical models firmly grounded in fundamentals was stressed. Porous media models are characterized by extreme disparities in physical scale, from that of an individual pore to the entire region, and properly accounting for these scales is a challenge in model development. In both air and land discussions, the importance of tests of models in actual field situations was pointed out, while in the discussion of the physical processes-water papers the importance of formulating mathematical models to aid in effectively planning field experiments was noted.

Chemical Processes - Introduction

Philip C. Singer
Department of Environmental Science and Engineering
University of North Carolina
Chapel Hill, NC 27599-7400

We live in a world of chemicals. Since World War II, we have experienced a virtual chemical revolution on this planet. Industry has generated hundreds of thousands of new chemicals to satisfy the apparent needs of society.

Waste is an inherent by-product of this revolution. Despite classical methods of waste treatment, we are finding that our water, air, and land is becoming contaminated with chemical wastes. Many of these chemicals result in severe adverse impacts on human health, on ecosystems, and even on our climate. Society has become familiar with the likes of PCBs, dioxins, chlorofluorocarbons, trihalomethanes, and vinyl chloride.

The responsibility of the environmental engineering profession has changed in recent times. There is an increasing need for us to interact with other scientists and engineers to become better versed and more familiar with the thermodynamic and kinetic principles governing the speciation, partitioning, transformations, transport and fate of contaminants in the environment, and processes for their control.

The subject of environmental chemistry and chemical processes is a very broad one. In order to address the subject of chemical processes in the air, land, and water environments in a more focused fashion, each of the speakers selected for this session was asked not to present a catalog of research needs in the subject area of his talk, but rather to focus on the specific research that he would like to conduct in the next 5 to 10 years. In this manner, it was hoped that more focused ideas would emanate from the talks, and that more focused discussions would be generated.

Dr. Michael Hoffmann of the California Institute of Technology was asked to lead the discussion of 'Chemical Processes - Air' because of his active research program in atmospheric chemical kinetics and the central role such kinetics play in local and global environmental and climatological phenomena. Dr. William Glaze, formerly of UCLA and currently at the University of North Carolina at Chapel Hill, was asked to make the presentation on 'Chemical Processes - Land' because of the growing problems in contamination of the subsurface environment and his research involving advanced oxidation processes for the treatment of groundwater. Dr. Charles O'Melia of Johns Hopkins University was invited to lead the discussion of 'Chemical Processes - Water' because of his active research in aquatic surface chemistry and the central role that such surfaces play in the transformation, transport, and fate of chemicals in the aquatic environment.

Atmospheric Chemistry

Michael R. Hoffmann
Environmental Engineering Science
California Institute of Technology
Pasadena, California 91125

Some research problems in the area of atmospheric chemistry are of contemporary concern and have significant societal impacts such as acidic deposition and its associated ecological and materials effects, depletion of the ozone layer and formation of the Antarctic ozone hole, global climate change due to CO_2 and CH_4 increases in the atmosphere, the incineration of hazardous wastes, and urban and regional-scale photochemical smog. Photochemical smog was once thought to be exclusively a problem for Southern California. However, "LA smog" has become a world-wide problem associated with large-scale urbanization. Increased combustion of fossil fuels over the last century has resulted in a steady rise in the global atmospheric CO_2 concentration. The increase in CO_2 and other "greenhouse gases" such as CH_4, N_2O, and the chlorofluorocarbons is predicted to result in a global warming trend, which may have severe consequences for society. Likewise, the increase in the chlorofluorocarbons in the upper atmosphere has been associated with the measured decrease in our protective ozone layer and in the formation of the Antarctic ozone hole. Incineration of hazardous wastes may become essential since alternatives such as land disposal are proving to be untenable.

Atmospheric chemistry can be broken down into phenomena that occur on a local, regional, or global scale in either the gas, aqueous, or particulate phase. The alteration of the chemical composition of some components of the atmosphere has resulted in significant problems. Some of the problems are regional or local in extent such as acidic deposition and urban photochemical smog while other problems or phenomena are global in nature. They include the depletion of stratospheric ozone, climate modification due to CO_2 release, alterations in the oxidative capacity of the global troposphere, and alteration of the global biogeochemical cycles of sulfur, nitrogen, phosphorus, and carbon.

General subject areas for research in atmospheric chemistry include:

1. The development of large-scale mathematical models of the atmosphere that include sources and sinks of atmospheric species, chemical transformations, radiative interactions, and transport.
2. Gas-phase chemical kinetics, photochemistry, and spectroscopy of important chemical components in the atmosphere (e.g. H_2O, O_3, NO, NO_2, H_2S, ClO, ClO_2, OClO, CH_4, RSH, RSSR, CS_2, hydrocarbons, PAN, CO, N_2O_5).
3. Multiphasic chemistry and photochemistry: clouds, rain drops, haze aerosol, dry aerosol, ice,

supercooled water, soot, and gas clusters.

4. The chemistry and biochemistry of sources and sinks for atmospheric species (e.g. N_2, NH_3, $(CH_3)_2S$, H_2S, SO_2, COS, CO_2, CH_4).
5. Measurement of atmospheric species (e.g. OH, HO_2, RO, RO_2, NO_3, HNO_2, HNO_3, N_2O_5, PAN, ClO, HCl, ROOH, NH_3, RCOOH, ROOH, H_2O_2, H_2SO_4, RH).

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1. Reactions of Aldehydes with SO_2 in Clouds

Aldehydes (RCHO) and SO_2 react in the aqueous phase to form stable α-hydroxyalkylsulfonic acids ($RCH(OH)SO_3H$). The three major consequences of this reaction which is known to occur in tropospheric droplets such as fog, clouds and rain are, a) an increase in proton acidity brought on by dissociation of the strong sulfonic acid; b) an increase in the total dissolved [S(IV)] within the droplet, i.e. an increase in the sum of $H_2O{\cdot}SO_2 + HSO_3^- + SO_3^{2-} + RCH(OH)SO_3^-$; and c) the stabilization of the S(IV) oxidation state even in the presence of oxidants, with a concommitant delay in the oxidation to S(VI) (H_2SO_4). Thus this apparently simple addition reaction has significant environmental implications and may have an impact on the fate and transport of SO_2 on a global scale. Carbonyls and SO_2 may both have natural as well as anthropogenic sources.

The oxidation of naturally-occurring CH_4 by ·OH leads to background levels of 0.5 to 2 ppb of formaldehyde. Observations of HCHO at remote sites are generally consistent with predictions of background concentrations supported by oxidation of natural CH_4 emissions. Biogenic hydrocarbons, for example the natural emissions of wet tropical forests, are thought to lead to the formation of other aldehydes. The terpenes, isoprene and α-pinene, are rapidly oxidized by ·OH and O_3 to yield carbonyl species such as formaldehyde, acrolein ($CH_2{=}C(CH_3)CHO$), methylglyoxal (CH_3COCHO), and methylvinylketone ($CH_2{=}CHCOCH_3$) as well as other more complex aldehydes and ketones. There is also the possibility that continental and marine biogenic emissions of gaseous reduced sulfur compounds such as H_2S and $(CH_3)_2S$ may be a source of SO_2 (by tropospheric oxidation) and thus in remote clouds the formation of α-hydroxyalkylsulfonic acids is a distinct possibility.

The mechanism for the formation S(IV)-aldehyde adducts appears to proceed via the nucleophilic attack of either sulfite or bisulfite ions on the carbonyl carbon of an aldehyde. Due to the greater reactivity of SO_3^{2-}, the addition reaction proceeds more rapidly at high pH where SO_3^{2-} is the predominant form of S(IV). In some cases, however, reaction rates may be limited by dehydration of the aldehyde gem-diol, or be subject to specific acid catalysis. Hydroxyalkylsulfonates are thermodynamically stable between pH 2 and 8 with formation constants typically in the range of 10^3 to 10^9 M^{-1}. Classes of aldehyde thought to be important in the atmosphere include aliphatic and aromatic monocarbonyls, hydroxycarbonyls, dicarbonyls, ketones, and α-ketoacids.

While the general mechanism for adduct formation is fairly well understood, few experimental determinations of rate constants for stability constants for other S(IV) adducts with the above classes of aldehydes, ketones, and ketoacids are currently unavailable.

TABLE 1. **Important Species in Atmospheric Chemistry.**

A. Global Climate Change (*spectroscopic properties & distributions*)

1. Greenhouse Gases: CO_2, O_3, CH_4, N_2O, $CFCl_3$, CF_2Cl_2, H_2O

2. Aerosol & Cloud: SO_2, RCHO, RCOOH, $(CH_3)_2S$, H_2SO_4, HNO_3, SO_4^{2-}, RSO_3^-, NH_4^+, CH_3SO_3H

B. Biogeochemical Cycles (*sources, sinks, & chemical transformations*)

1. Carbon: CO, CO_2, CH_4, CH_3O_2, CH_2O, C_2H_6, C_5H_8, $C_{10}H_{16}$

2. Nitrogen: N_2O, NO, NO_2, NO_3, N_2O_5, HNO_3, HNO_2, $CH_3COO_2NO_2$

3. Sulfur: H_2S, $(CH_3)_2S$, $(CH_3)_2S_2$, CH_3SH, CS_2, OCS, SO_2, CH_3SO_3H, $HOCH_2SO_3H$

4. Ammonia: NH_3, NH_2, NH_4NO_3, NH_4HSO_4

5. Oxidants: HO_2, H_2O_2, OH, O_3

C. Stratospheric Ozone Depletion (*photochemistry, sources & distribution*)

1. Oxygen: O_3, $O(^3P)$, $O_2(^1D)$, $O_2(^1\Delta g)$

2. Hydrogen: H_2O, H, OH, HO_2, H_2O_2

3. Nitrogen: N_2O, NO, NO_2, NO_3, N_2O_5, HNO_2, HO_2NO_2

4. Carbon: CH_4, CH_3, CH_3O, CH_3OO, CH_3OOH, CH_2O, CHO, CO, CO_2

5. Halogen: CH_3Cl, CF_2Cl_2, $CFCl_3$, CCl_4, Cl, HCl, ClO, OClO, ClOO, HOCl, $ClONO_2$, Cl_2O_2, CH_3Br, Br, BrO, HBr, $BrONO_2$

6. Sulfur: OCS, SO_2, HSO_3, H_2SO_4

D. Atmospheric Oxidants

1. Oxygen: O_3, $O(^3P)$, $O(^1D)$, $O_2(^1\Delta g)$, H_2O_2

2. Radicals: HO, HO_2, Cl, ClO, RO_2, RCO_3, NO_3, IO,

E. Classes of Chemicals of Interest

1. Carbon Oxides: CO_2, CO, H_2CO_3

2. Methane Derivatives: CH_4, CH_3, CH_2O, RCHO, CH_3O, CH_3OOH, $CH_3O_2NO_2$

3. Complex Hydrocarbons: C_5H_8, $C_{10}H_{16}$, $R(CH_2)_nCOOH$, $OHC(CH_2)_nCHO$, ROH, C_xH_y

4. Reactive Oxygen: O_3, $O(^3P)$, $O(^1D)$, $O(^3D)$, $O^2(^1\Delta g)$, H_2O_2, $O_2(^1\Sigma\ g)$, O_2

5. Hydrogen/Hydrogen Radicals: H_2O, H, OH, HO_2, H_2O_2, H_2

6. Nitrogen Oxides: N_2O, NO, NO_2, NO_3, N_2O_5, HNO_2, HNO_3, HO_2NO_2

7. Sulfur Compounds: H_2S, $(CH_3)S$, $(CH_3)_2S_2$, CH_3SH, CS_2, OCS, SO_2, H_2SO_5, $CH_3COCH(OH)SO_3H$, CH_3H, CH_3SO_3H, CH_3SO_3H, $HOCH_2SO_3H$, SO, HSO_3

8. Chlorofluorocarbons: CH_3Cl, CF_2Cl_2, $CFCl_3$, CCl_4, Cl, HCl, ClO, OClO, ClOO, HOCl, $ClONO_2$, Cl_2O_2

9. Bromine Species: CH_3Br, Br, BrO, HBr, $BrONO_2$

10. Iodine Species: HI, IO, $IONO_2$

11. Metals Compounds: Na, NaO_2, NaOH, NaCl

12. Aqueous Species: HCO_3^-, CO_3^{2-}, SO_4^{2-}, NO_3^-, RCO_2^-, HSO_3^-, NH_4^+, Cl^-, OH^-, OH, HO_2, HCHO, RCHO, $(CHO)_2$, O_3, Fe(III), Mn(II), Na^+, Ca^{2+}, Mg^{2+}, HSO_4^-

13. Radionuclides: ^{222}Ra, ^{85}Be, ^{9}Be, ^{2}D, ^{3}T, ^{210}Pb, ^{137}Cs

14. Isotopes: ^{14}C, ^{18}O, ^{13}C, ^{33}S

Table 1 provides an overview of important chemical species in the atmosphere. Some important research topics related to these are described below.

References to 1

J.W. Munger, C. Tiller, and M.R. Hoffmann, *Science*, 231, 247-249 (1986).

T.M. Olson and M.R. Hoffmann, *J. Phys. Chem.*, 92, 533-540, 4246-4253 (1988).

E.A. Betterton, Y. Erel, and M.R. Hoffmann, *Environ. Sci. Technol.*, 22, 92-99 (1988).

2. Chemistry of Stratospheric Ozone Depletion

The depletion of ozone in the Antarctic stratosphere has been observed in the spring over the last 6 years. A number of theories have been proposed to explain the apparent loss of ozone. They include physical explanations such as the dynamical uplifting of the lower stratosphere and chemical mechanisms involving catalytic free-radical cycles with halogen radicals as chain carriers. The halogen free radical initiators are produced by the photolysis of anthropogenic chlorofluorocarbons. One possible cycle is

$$CF_2Cl_2\ (h\upsilon)\text{----->}\ CF_2Cl + Cl\cdot$$

$$HOCl\ (h\upsilon)\text{----->}\ OH + Cl\cdot$$

$$2\{Cl\cdot + O_3\ \text{----->}\ ClO + O_2\}$$

$$ClO + ClO\ \text{----->}\ Cl_2O_2$$

$$Cl_2O_2 + M\ \text{----->}\ Cl_2 + O_2 + M$$

$$Cl_2\ (h\upsilon)\ \text{----->}\ 2\ Cl\cdot$$

where M is a third-body molecule and hυ is a photon, to give a overall net reaction of

$$2\ O_3\ \text{----->}\ 3\ O_2$$

The homogeneous theories require large amounts of active chlorine to be liberated from reservoir species such as HCl or chlorine nitrate, $ClONO_2$. In addition low levels of NO_2 are required to prevent scavenging of the chain carrier, ClO, as inactive $ClONO_2$,

$$ClO + NO_2 \text{ -----> } ClONO_2$$

These conditions can be obtained if the following heterogeneous reactions occur on the surfaces of polar stratospheric clouds, which are thought to consist mainly of ice and nitric acid, HNO_3.

$$ClONO_2 + HCl \text{ (ice)-----> } Cl_2 + HNO_3$$

$$ClONO_2 + H_2O \text{ (ice)-----> } HOCl + HNO_3$$

Recent research has shown that the reaction rate between HCl and $ClONO_2$ is greatly enhanced in the presence of ice particles. Chlorine, Cl_2, is released into the gas phase on a time scale of several milliseconds, while HNO_3 remains in the ice. These reactions are able to release photolytically active chlorine from its most abundant reservoir species and promote the formation of HNO_3, which removes NO_2 from the gas phase. Thus the conditions for the efficient catalytic destruction of ozone by halogenated free radicals are provided by the polar stratospheric clouds.

Further research should be focused on the rate of formation of Cl_2O_2 and more detailed investigation of the heterogeneous and physical processes involving ice crystals and $ClONO_2$ and N_2O_5. Experimental approaches involve use of flash photolysis resonance fluorescence, later magnetic resonance, high pressure turbulent flow reactors, FTIR, and mass spectrometry to obtain elementary reaction rate constants and to detect and measure unstable species such as HO_2NO_2, HOCl, and $ClONO_2$.

References to 2

M.J. Molina, T. Tso, L.T. Molina, and F. Wang, *Science*, 238, 1253-1257 (1987).

M.J. Molina and L.T. Molina, *J. Phys. Chem.*, 91, 433 (1987).

M.A. Tolbert, M.J. Rossi, R. Malhotra, D.M. Golden, *Science* 238, 1258-1260 (1987).

3. The Atmospheric Chemistry of Organic-sulfur Compounds

The gas phase chemistry of organo-sulfur compounds plays an important role in the global sulfur cycle, the formation of sulfur aerosol in marine air, the atmospheric fate of biogenic organo-sulfur emissions, and the acidity of precipitation in remote areas. The oxidation of organo-sulfur compounds produces SO_2, alkane sulfonic acids (RSO_2OH) and H_2SO_4. Organo-sulfur compounds such as thioalkanes (RSH), alkyl sulfides (RSR), and alkyl disulfides (RSSR) react rapidly with OH. The mechanism of the initial OH attack is not firmly understood. The reaction may proceed via addition, abstraction, or intermediate adduct formation. For example, OH oxidation of dimethyl sulfide may occur by abstraction.

$$CH_3SCH_3 + OH \text{ -----> } CH_3SCH_2 + H_2O$$

or by addition

$$CH_3SCH_3 + OH \text{ -----> } CH_3S(OH)CH_3 \text{ -----> } CH_3 + CH_3SOH$$

followed by reactions of thiyl radical, CH_3S

$$CH_3S + O_2 \text{----->} CH_3SO_2 \text{----->} CH_3 + SO_2$$

$$CH_3S + NO \text{----->} CH_3SNO$$

$$CH_3 + NO_2 \text{----->} CH_3SNO_2$$

Oxidation of sulfenic acid, CH_3SOH leads to form the corresponding alkane sulfonic acid.

$$CH_3SOH + O_2 \text{----->} CH_3SO_2OH$$

The alkyl radical CH_3SCH_2 is expected to yield CH_3 and HCHO.

The critical uncertainties in these reaction pathways that need to be explored include: 1) the nature of the initial OH attack (i.e. addition vs abstraction), 2) the competition among the various reactions listed above for the radical intermediates and consequently the relative yield of SO_2/SO_4^{2-}, 3) the relative importance of RSOH + O_2-----> and other pathways leading to the formation of alkane sulfonic acids, 4) the distribution of alkane sulfonic acids between the gaseous and condensed phases, 5) the dependence of RSO_3H saturation concentrations on humidity, and 6) the relative importance of reaction with OH vs. other removal processes such as direct photolysis or by reaction with NO_3.

References to 3

F.D. Yin, D. Grosjean and J.H. Seinfeld, *J. Geophys. Res.*, D91, 14417-14438 (1986).

S. Hatakeyama and H. Akimoto, J. Phys. Chem. 87, 2387-2395 (1983).

A.J. Haynes, P.H. Wine, and D.H. Semmes, *J. Phys. Chem.*, 90, 4148 (1986).

4. Kinetics and Mechanisms of Free Radical Reactions Important in the Troposphere and Stratosphere

The importance of free radical chemistry in the atmosphere was first recognized more than 50 years ago. In recent years, atmospheric chemical research has been focused on reactions of HO_x, NO_x, Cl_x, Br_x and SO_x species. Model calculations have demonstrated clearly that our understanding of the complicated chemistry of the troposphere and stratosphere is far from complete. For example, significant discrepancies remain between observations and predictions of absolute O_3 concentrations and the short term variability in ClO concentration profiles in the stratosphere. Often model calculations invoke reactions for which little kinetic data are available. Furthermore, disagreements among investigators about the results of experimental kinetic studies are common. More research is needed to measure absolute rate constants, product yields, and absorption cross sections by direct and unambiguous methods for reactions of importance in atmospheric chemistry. Reactions of interest are listed in Table 2. Experimental techniques to study these reactions include: flash photolysis/UV absorption, discharge flow/FTIR and diode array IR, discharge-flow resonance fluorescence, GC, GC/MS, flowing afterglow-chemiluminescence, laser induced fluorescence (Nd-YAG pumped dye laser), and discharge-flow mass spectrometry/resonance fluorescence.

5. Determination of the Chemical Reaction Pathways for Alteration of the Atmospheric Organic Aerosol

Measurements made of the chemical composition of the airborne particulate matter in the atmosphere typically show that about one-third of the atmospheric particle burden is contributed by organic compounds. These airborne particles lead to visibility reduction, and many of the organics found on aerosols are known carcinogens and mutagens. Source emissions of organics to the atmosphere need to be measured in a consistent fashion across a wide variety of the source types that eventually lead to organic particles. Dilution source

Table 2. Radical Reactions of Importance in Stratospheric and Tropospheric Chemistry

Stratospheric and Tropospheric Reactions

$HO_2 + O_3 \text{----->} OH + 2\,O_2$
$ClO + ClO \text{----->} Cl + OClO$
$ClO + ClO \text{----->} Cl_2 + O_2$
$ClO + ClO \text{----->} Cl + ClOO$
$ClO + ClO + M \text{----->} (ClO)_2 + M$
$ClO + BrO \text{----->} Br + Cl + O_2$
$ClO + BrO \text{----->} Br + OClO$
$ClO + OH \text{----->} HO_2 + Cl$
$ClO + OH \text{----->} HCl + O_2$
$H + HO_2 \text{----->} OH + OH$
$H + HO_2 \text{----->} O + H_2O$
$H + HO_2 \text{----->} H_2 + O_2$
$H + H_2O_2 \text{----->} OH + H_2O$
$H + H_2O_2 \text{----->} H_2 + HO_2$
$O + HO_2 \text{----->} OH + O_2$
$HO_2 + HO_2 \text{----->} H_2O_2 + O_2$
$Cl + HO_2 \text{----->} HCl + O_2$

Tropospheric Reactions

$CH_3O_2 + HO_2 \text{----->} CH_3OOH + O_2$
$HCHO + HO_2 \text{----->} \text{products}$
$CH_3CO_3 + NO \text{----->} CH_3CO_2 + NO_2$
$CH_3CO_3 + NO_2 \text{----->} CH_3CO_3NO_2$
$OH + CS_2 \text{<----->} HOCS_2$
$HS + O_3 \text{----->} HSO + O_2$
$HSO + O_3 \text{----->} HS + 2O_2$
$HSO + O_2 \text{----->} \text{products}$
$HSO + NO_2 \text{----->} \text{products}$
$HSO + HSO \text{----->} \text{products}$
$OH + C_2H_4 \text{----->} \text{products}$
$OH + C_3H_6 \text{----->} \text{products}$
$OH + C_4H_8 \text{----->} \text{products}$
$NO_3 + C_2H_4 \text{----->} \text{products}$
$NO_3 + C_3H_6 \text{----->} \text{products}$
$NO_3 + C_4H_8 \text{----->} \text{products}$

samplers can be used to collect samples that are representative of the aerosol organics as they exist after the emissions of hot exhaust gases have cooled by mixing with the free atmosphere. Microchemical methods can quantify both bulk parameters of the atmospheric aerosol (e.g. organic acids content) and that can also identify key compounds that are characteristic of different source types. The source samples and ambient samples differ chemically in many ways. For example, the ambient samples are depleted in some unsaturated organic compounds in the summer months. This suggests that atmospheric chemical reactions are acting to transform the organic aerosol during its transport through the atmosphere, possibly by ozone-olefin reactions. The objective of this type of research is to assess the reaction pathways and mechanisms for the heterogeneous gas-particle chemical reactions that act to transform directly emitted organic aerosols in the atmosphere.

Key References to 5

H.A. Gray, G.R. Cass, J.J. Huntzicker, E.K. Heyerdahl, and J.A. Rau, *Environ. Sci. Technol.* 20, 580-588 (1986).

M.A. Mazurek, B.R.T. Simoneit, G.R. Cass, and H.A. Gray, *Intern. J. Environ. Anal. Chem.* 29, 119-139 (1987).

6. Mathematical Modeling of Atmospheric Chemical Processes

Atmospheric chemical reactions produce not only the regulated and often studied pollutants such as ozone and NO_2, but also a variety of unregulated and seldom studied species including the adehydes, organic acids and hydrogen peroxide. Comprehensive mathematical models for chemical reaction and transport of atmospheric pollutants recently have been employed by research groups to study the formation and transport of nitric acid and aerosol nitrates. These models can be further extended to investigate the formation, transport and chemical reactions with the earth's surface that are crucial to determining the atmospheric abundance and fate of the aldehydes, organic acids and hydrogen peroxide. Key questions that can be investigated include 1) the extent to which the aldehydes are directly emitted from combustion sources vs. formed in the atmosphere by chemical reaction, and 2) the circumstances under which organic acids formation is competitive with inorganic acids (e.g. HNO_3) formation as a source of atmospheric acidity. As future emission controls for reactive hydrocarbons (RCH) and oxides of nitrogen (NO_x) are planned as part of the nation's ozone control efforts, the effect of altered levels of RHC and NO_x on the production of organic acids, aldehydes and H_2O_2 in the atmosphere will be studied.

References to 6

A.G. Russell, G.J. McRae, and G.R. Cass, *Atmos. Environ.*, 17, 949-964, (1983).

A.G. Russell, G.J. McRae, and G.R. Cass, *Atmos. Environ.*, 19, 893-903, (1985).

A.G. Russell and G.R. Cass, *Atmos. Environ.* 20, 2011-2025, (1986).

7. Photochemical Formation of Hydrogen Peroxide and Organic Peroxides in Colloidal and Particulate Suspensions

Hydrogen peroxide, H_2O_2, has been found in virtually all aquatic environments at significant concentrations. Recent measurements of H_2O_2 in polar ice samples clearly show that H_2O_2 was abundant in the atmosphere for more than a thousand years. Hydrogen peroxide can be generated in the gas phase due to the combination of hydroperoxyl radicals, $HO_2^{\cdot}$, at the air-water interface due to photoinduced redox processes, and in the aqueous phase via photo-catalyzed reactions with humic/fulvic acid and green algae as mediators. Furthermore, $HO_2^{\cdot}$ radicals, which are produced in the gas phase, can be scavenged by the water droplets where they disproportionate to form H_2O_2. *In situ* generation of hydrogen peroxide together with the H_2O_2 scavenged from the gas phase is thought to be the main source for the H_2O_2 accumulated in cloudwater droplets. Hydrogen peroxide appears to be the principal oxidant of SO_2 in acidic clouds.

In addition to these pathways for H_2O_2 formation, other mechanisms are possible. For example many metal oxides, some of which are abundant in the environment, have been shown to act as photocatalysts for a wide variety of reactions such as the photo-assisted reduction of N_2 to NH_3 and the reduction of O_2 to H_2O_2.

Organic peroxides constitute another important group of potential environmental oxidants. They have been detected in surface waters, on pine needles, and in rain- and cloudwater. While their formation in the atmosphere has been established, there are few reports in the literature of their formation in the aqueous phase. The mechanistic and quantitative aspects of the appropriate photochemical processes occurring in natural waters are not clearly understood.

References to 7

D.W. Bahnemann, C. Kormann and M.R. Hoffmann, *J. Phys. Chem.* 91, 3789-3798 (1987).

A.P. Hong, D.W. Bahnemann and M.R. Hoffmann, *J. Phys. Chem.* 91, 2109-2117 (1987).

A.P. Hong, D.W. Bahnemann and M.R. Hoffmann, *J. Phys. Chem.* 91, 6245-6251 (1987).

C. Kormann, D.W. Bahnemann and M.R. Hoffmann, *Environ. Sci. Technol.* 22, 798-806 (1988).

8. Combustion and Incineration Chemistry

Pollutant emissions from combustion systems have been substantially reduced in recent years through the development and application of new combustion technologies. High efficiency combustion systems offer the possibility of complete detoxification of hazardous materials by conversion to carbon dioxide, water, and contaminants such as hydrochloric acid vapor that can be removed from the exhaust gases. Incineration can, in principle, be applied to virtually any organic waste material, making the development of incineration technologies highly desirable for the vast numbers of specialty chemical products and industries. Destruction removal efficiencies in excess of 99.9999% have been reported in tests of a number of prototype systems. High conversion efficiency and applicability to a broad range of materials make incineration attractive as a solution to hazardous waste disposal.

Factors that influence the destruction efficiency include: local temperatures and gas composition, residence time, extent of atomization of liquid wastes and dispersion of solid wastes, fluctuations in the waste stream composition and heating value, combustion aerodynamics, and turbulent mixing rates. Moreover, the waste materials to be incinerated are considerably more variable than are typical fossil fuels. The composition and even the heating value of the fuel entering an incinerator can vary dramatically and rapidly. Liquid wastes may contain both water and combustible organics. Imperfect mixing of such feedstocks can seriously impair combustion and, therefore, destruction efficiencies. The physical form of the waste material may also influence its conversion. For example, dioxin may survive intact through incineration up to 1150°C if it is bound to particulate matter.

The development of environmentally-acceptable incineration technologies for the disposal of hazardous wastes is dependent upon an understanding of: *(i)* atomization or method of introduction of the waste materials, *(ii)* evaporation and condensed phase reactions of the waste droplets in the incinerator environment, *(iii)* turbulent mixing in the incinerator, *(iv)* the kinetics of the thermal degradation and oxidation, *(v)* heat transfer in the incinerator, *(vi)* metal partitioning between vapor and particles and its dependence on inlet metal speciation, fuel composition, additive composition and combustion conditions, and *(vii)* the extent to which the fate of trace and heavy metals can be predicted by current equilibrium, kinetic, and aerosol dynamic models.

Experimental systems that can be used for the study of the evaporation and reaction of liquid and solid wastes and of the capture of toxic byproducts include bench scale studies and studies in larger laboratory combustion facilities. The evolution of a single particle can be studied using the electrodynamic balance, a device in which a single charged particle can be levitated for extended periods of time in a controlled environment and without contact with any foreign surfaces. FTIR and Raman spectroscopy can be used to follow reactions of single levitated particles. By studying single particles, the uncertainties introduced into studies of sprays by particle-to-particle variations in size or composition are minimized.

The influence of the reaction atmosphere, heat flux, and droplet properties need to be explored in order to gain a fundamental understanding of the chemical and physical processes that take place in the incineration environment.

References to 8

M.D. Cohen, R.D. Flagan, and J.H. Seinfeld, *J. Phys. Chem. 91* 4563-4574 (1987).

M.D Cohen, R.C. Flagan, and J.H. Seinfeld, *J. Phys. Chem. 91* 4575-4582 (1987).

P.S. Northrup, G.R. Gavalas, and R.C. Flagan, *Langmuir 3*, 300 (1987).

G.S. Grader, R.C. Flagan, S. Arnold and J.H. Seinfeld, *J. Chem. Phys. 86*, 5897-5903 (1987).

W.P. Linak, J.A. McSorley, J.O.L. Wendt and J.E. Dunn, *J. Air Pollution Control Assoc. 37*, 935-942 (1987).

W.P. Linak, J.A. McSorley, J.O.L. Wendt and J.E. Dunn, *J. Air Pollution Control Assoc. 37*, 54-65 (1987).

Discussion: Atmospheric Chemistry

Harvey E. Jeffries
Department of Environmental Sciences and Engineering
School of Public Health
University of North Carolina
Chapel Hill, NC, 27599

Hoffmann outlined an impressive array of fundamental research extending in scale from reactions occurring at the surface of a single particle to reactions occurring over thousands of square kilometers in the Antarctic, and including reactions among gas, liquid, and solid phases. He described research involving measurements, process elucidation, and mathematical modeling. I will emphasize how some of these topics relate to national environmental policy.

To influence national environmental policy in the next five years, the atmospheric chemistry community needs to exhibit significant advancement in a few specific areas. First, to maintain a solid scientific basis for the nation's air quality control policy for secondary pollutants such as ozone and other oxidants, the atmospheric kinetics community needs to make significant progress in understanding and describing the atmospheric oxidation of aromatic compounds. Second, to understand the implications of alternatives in control strategies for urban and tropospheric ozone and oxidant levels, the biological, atmospheric kinetics, and mathematical modeling communities need to quantify the roles of biogenic hydrocarbons verses that of anthropogenic hydrocarbons and oxides of nitrogen in producing and maintaining boundary layer and tropospheric oxidants. Third, to determine appropriate and effective control measures for acid deposition effects, the atmospheric sciences community needs to increase its understanding of the role of cloud dynamics and cloud chemistry in ventilating the boundary layer and in transforming emissions into secondary pollutants, and then to incorporate this improved understanding into control models. Fourth, the extent to which, and the mechanisms whereby, man's emissions and other actions are modifying the global chemistry of the troposphere need quantifying. Finally, much more efficient methods for incorporating complex chemistries into a whole range of simulation models covering the spatial and temporal scales from urban to global chemical tracer models are needed to allow for the scientific exploration of policy options for delaying or slowing global climate change. Significant progress in any one of these five areas could have a major influence on environmental policy or on the selection and implementation of control strategies.

Based upon EPA analysis of more than 800 samples in 46 U.S. cities over three years, toluene is the most ubiquitous compound in the urban atmosphere, occurring between 1st and 20th in concentration in every sample. The atmospheric sink for toluene is its reactions with hydroxyl (HO·) radicals. Knowledge of subsequent reactions after HO· attack, however, is very poor and has been the subject of a number of investigations which have not succeeded in producing an acceptable mechanism, in part, because the product carbon balance has been poor (between 60-80% in the best studies). The representation of this chemistry in models for air quality prediction remains *ad hoc*, whereas extensive progress has been made in understanding and representing the urban atmospheric chemistries of alkanes, alkenes, and carbonyls. Difficulties in representing aromatic chemistries weaken the credibility of control model predictions and sometimes have lead policy makers to wish for a simpler tool.

The relative roles of biogenic and anthropogenic hydrocarbons and oxides of nitrogen in producing regional ozone remains uncertain. Some groups of researchers continue to suggest that, because of the supposedly large natural sources of hydrocarbons, the government's commitment to volatile organic compound control strategies as opposed to oxides of nitrogen control strategies is doomed to failure. This discussion has occurred for more than 20 years, but increased interest in regional and global tropospheric ozone changes is raising the policy question again.

The influence of the regional moisture field on atmospheric chemical transformations and the role clouds may play in rapidly transporting boundary layer chemicals to the free troposphere are believed to be major factors in the ability to predict the consequences of various expensive decisions to abate acid deposition. These processes may be so important that incorrect representations may lead to ineffective policy decisions.

Atmospheric measurements of trace gas concentrations offer the most compelling evidence that man is changing the global composition of the atmosphere. That these changes are significant and may result in unexpected feedback is more difficult to establish. The correct assessment of these effects will require acceptable treatment of coupled atmospheric chemical transformations on a range of temporal and spatial scales never tried before, encompassing time scales from days to a century and spatial scales from rain drops to the globe. The next five years may see the ground work for such an effort put into place by Congress.

Chemical Processes - Land

William Glaze
Formerly: School of Public Health
University of California Los Angeles, Los Angeles, CA 90024

Currently: Department of Environmental Sciences and Engineering
University of North Carolina, Chapel Hill, North Carolina 27599

Our purpose in this Conference is to identify approaches for managing and controlling environmental problems. This paper will relate to problems in the area of Chemical Processes that occur in the "land" environment.

Of such processes, several appear to be relevant to this conference. They are:

1. Chemical processes that occur in soils during and after precipitation events (especially acidic precipitation).
2. Chemical processes that occur when agricultural chemicals are placed on and into the land.
3. Chemical processes that occur in the soil as a result of the disposal of chemicals, either intentionally or by error.
4. Chemical processes that may be used to treat soil so as to remove excessive chemical contaminants.

Given the time allowed for my presentation, and the scope of my expertise, I will focus only on the latter issue.

Introduction

The handling and treatment of contaminated soils, as well as sludges and other semi-solids from waste treatment facilities, has taken on different dimensions during the past two decades with the passage of new legislation. The regulations that are being promulgated require that these materials be non-"toxic", otherwise they must be disposed of according to strict rules. The associated liability and costs are forcing U.S. industry to minimize the generation of hazardous wastes and to remedy any sources of contamination that already exist. Superfund legislation has authorized the EPA to proceed with assessment and clean-up of abandoned sites, and if possible to charge responsible parties for the associated costs.

There are important research questions that remain in the area of chemical processes in soils that have immediate relevance to the management of hazardous wastes. Two of these are:

A. Questions associated with "How Clean is Clean?"; that is, when is a soil, sludge, etc. clean enough to be considered safe for the intended purpose (transport, disposal, reuse)? This is in part a political question, but there are also scientific issues that are involved.

B. What technologies are available for treatment of these materials in order to remove hazardous materials below regulatory limits?

To illustrate some aspects of these problems that will drive future research, we will focus on organic contaminants in soils, sludges and other similar materials. Inorganic and radiological contaminants are also important from a regulatory point of view and raise similar research questions.

"How Clean is Clean?"

Among the most interesting research questions associated with How Clean is Clean is the identification and monitoring of substances in soils, sludges, etc. so that a true assessment can be made of the risk associated with the material. Current approaches usually involve several approximations. One of these is the use of analytical protocols and risk assessment procedures that focus on a limited number of compounds while neglecting others that might be equally hazardous. This is due in part to difficulties in the analysis of some classes of compounds. Compounds that have resisted protocol development include polar compounds, compounds that resist typical preconcentration methods (e.g. strong acids or bases), and compounds that do not perform well in gas chromatography systems. As an example of the magnitude of this problem, one hundred and fifty chemicals were dropped from the RCRA Appendix 8 list in the formation of Appendix 9. A major factor in the decision to do so was the lack of certified analytical methods for many of these compounds, probably a majority.

Research in this area must focus on methods that will extend our capability to characterize hazardous materials more completely. Methods which seem to offer the most promise are HPLC, HPLC/MS, MS/MS, FTIR/MS and other hyphenated methods. In addition, more research is needed on the application of these and other methods to complex matrices.

Treatment Methods for Decontamination of Soils, Sludges, etc.

Treatment methods for handling soils are primitive at best. An examination of the literature reveals few published works in which careful studies have been carried out to evaluate treatment options. Most of the treatment technologies which are currently being used have come from the private sector and have not been thoroughly evaluated by objective parties, nor are their mechanisms very well understood.

Chemical treatment options for removal of organic materials from soils, sludges, etc., can be classified as one of the following: (1) solvent extraction processes, (2) oxidation processes, and (3) reduction processes. Solvent extraction processes have not received very much attention since they involve the prospect of using environmentally damaging solvents in large quantities, except in the case of steam stripping.

Reduction processes are relatively few in number, although one process, the use of potassium in combination with polyglycols, seems to be useful for the dechlorination of halogenated organics. To our knowledge, this process has not been thoroughly investigated in terms of its mechanism.

Oxidation processes involve several possibilities, including combustion, high-temperature/pressure wet air oxidation, and Advanced Oxidation Processes. Of these, combustion seems to be the most popular process at the present time, but it is costly, especially in dealing with large quantities of soil, sludges, etc.

We are involved in the study of Advanced Oxidation Processes, redox processes that appear to hold promise for the treatment of soils, sludges, etc., as well as aqueous solutions. Our present work is of a more basic nature, dealing primarily with aqueous systems, but industrial users seem to be applying these processes to a variety of materials of increasing complexity.

The Chemistry of Advanced Oxidation Processes

We define advanced oxidation processes as those which involve the generation of highly reactive oxyspecies, namely the hydroxyl radical. Hydroxyl radicals have exceptionally large rate constants with organic compounds of many different types, generally in the range of 10^{9-10} $M^{-1}s^{-1}$. Hydroxyl radicals also react with many anions in electron transfer processes and the radicals that are produced, such as the carbonate radical, the sulfate radical, the nitrate radical, etc., are themselves fairly reactive reagents.

There are several engineering approaches to the generation of hydroxyl radicals. These include processes which involve combinations of ozone (and therefore dioxygen), hydrogen peroxide and ultraviolet radiation: O_3/H_2O_2, O_3/UV, O_3/UV, H_2O_2/UV. The prospects for application of methods that use UV do not appear very good; however, the O_3/UV process has been successfully used for treatment of several complex waste streams, including pesticide waste slurries. Processes that involve ozone and hydrogen peroxide are more promising. Also, hydrogen peroxide may serve as a precursor for hydroxyl radicals by an entirely different mechanism, namely metal catalysis. The best example of this is the well-known Fenton reaction, involving Iron (III) and hydrogen peroxide. Although this reaction has been known for many years, it has not been used in hazardous waste clean-up. Several firms and academic researchers are investigating these and similar processes and some demonstration projects are underway.

Combinations of Chemical and Biological Oxidation

Chemical and biological oxidation can very often be used in a complementary fashion in the treatment of materials which are highly resistant to biological treatment. Advanced oxidation processes such as those discussed above can render waste more biodegradable by partial oxidation. Ozone/UV followed by biological oxidation was investigated by Somich et al. for the treatment of pesticide wastes and by Jones et al. on oil shale retort waters. Organic compounds that are partially oxidized become more biodegradable and are more susceptible to direct treatment or benign treatment in soil matrices.

Research Goals

The goals of our present research program are:

1. to model selected Advanced Oxidation Processes, using fundamental chemical kinetic, mass transfer and photochemical principals.
2. to test these models in order to determine the range of applicability of the processes for the oxidation of different organic pollutants in different environmental matrices. The role of natural OH radical promoters and scavengers is critical.
3. to examine by-products of oxidation processes for selected organic pollutants and natural oxidation substances.
4. to examine processes that involve UV for treatment of wastes and waters.
5. to conduct exploratory studies on peroxidation processes.

Discussion: Chemical Processes - Land

Rene P. Schwarzenbach
Swiss Federal Institute for Water Resources and
Water Pollution Control (EAWAG)
8600 Dubendorf
Switzerland

Among the various aspects of human impact on the environmental compartment "land", chemical pollution of soils and aquifers is undoubtedly one of the key issues to be addressed, regardless of whether one likes to look upon soil as being a pivotal part of a terrestrial ecosystem or just as a welcome compartment for waste disposal. In his paper, Dr. William Glaze has chosen to confine himself to discussing approaches for (chemical) decontamination of soils and aquifers that are polluted with hazardous organic chemicals. Given the guidelines by the conference chairman, it is, of course, quite logical that Dr. Glaze focuses primarily on research that he would like to conduct within the next five years or so. However, since in the U.S., a significant part of the environmental research is carried out by environmental engineers, I would have liked to see a somewhat broader discussion of the issue "Chemical Processes: Land", at least on a general introductory level. I feel that, although research directed to develop strategies and methods for clean-up of contaminated soils, aquifers, and waste disposal sites is important and is requested by the public, we need to put our major research efforts in this field in further improving our understanding of the basic processes that lead to long-term alterations of the quality of soils and aquifers. Today, our ability to assess long-term risks connected to inputs of anthropogenic chemicals to soils and aquifers from, for example, atmospheric depositions, agricultural activities or from waste disposal is still rather poor. With respect to chemical processes (which are, of course, very often interrelated with physical and biological processes), particular emphasis should be given to reactions occurring at solid/water interfaces. Such processes include ion exchange, complexation, dissolution and precipitation reactions, as well as transformation reactions of natural and xenobiotic organic chemicals. Only a profound understanding of these processes and of their impact on a given soil or aquifer will enable us to take appropriate measures for future protection and/or remediation of such systems.

In his paper, Dr. Glaze proposes mainly two areas of research:

1. The development of analytical methods for determination of polar organic compounds including products from chemical oxidation of contaminated soils and aquifers, and
2. The application of advanced oxidation processes, in particular, the use of hydroxyl radicals for oxidation of organic pollutants in soils and aquifers.

I fully agree with Dr. Glaze's suggestions that analytical chemists should be encouraged (and supported) to continue in the development of methods for the qualitative and quantitative determination of polar organic compounds in environmental samples. Such methods are not only important in the context of the research proposed in his paper, but they are generally needed in the field of environmental science and engineering.

With respect to the application of advanced oxidation processes for the clean-up of contaminated soils and aquifers, I would like to raise a few questions. Since I am not an expert in this field, I wonder on what scale the application of such oxidation methods for soil and aquifer treatment is technically feasible. Furthermore, is it not a waste of resources to use a very non-selective and rather expensive oxidant to try to transform specific organic pollutants in a complex matrix such as soil? What fraction of the hydroxyl radicals produced will actually react with the pollutants, and not be scavenged by the matrix? Also, isn't there a good chance that non-selective oxidations of complex mixtures of chemicals will yield hazardous transformation products that are even more difficult to analyze, thus rendering the question "how clean is clean?" almost unanswerable? Would it not be more appropriate to use selective chemical oxidation methods, and apply such methods only to well defined problems? I would like to point out that the aim of these questions is to stimulate discussion.

In summary, I think that the paper presented by Dr. William Glaze raises interesting questions concerning the applicability of oxidation methods that, so far, have been primarily used in water treatment to the decontamination of soils (and possibly aquifers) that are polluted with organic chemicals. Of particular interest seems to be the perspective of using chemical oxidation methods followed by biological treatment of the oxidized material. However, when addressing future research issues covered by the topic "Chemical Processes: Land", we should be aware that treatment of contaminated soils and aquifers represents only one among many other important research directions in environmental engineering.

Chemical Processes - Water

Macromolecules at the Solid-Water Interface: Conformations and Consequences

Charles R. O'Melia
Department of Geography and Environmental Engineering
The Johns Hopkins University
Baltimore, Maryland 21218

Goal and Objectives

The goal of the author's research is to understand interfacial processes and to use this knowledge in studies of the functioning and the protection of the environment. The scientific focus of this research is the interfacial region that surrounds phases (solids, liquids, and gases) in aquatic, atmospheric, and terrestrial environments. The size of this region is characterized by the surface area of the phases in a system and by a thickness extending upward from a few angstroms. Knowledge of the stoichiometry, speciation, structure, and streamlines in this region is necessary for understanding many and perhaps most of the important processes in natural systems and in treatment technologies.

Study of the properties of environmental surfaces was begun at least a century ago as exemplified by the formulation of quantitative adsorption isotherms for polder soils in The Netherlands. The field has taken on new vigor and intensity in recent years for fundamental and practical reasons. The development of the field of environmental chemistry in the 1960's, new analytical techniques for the measurement of pollutants at trace concentrations, advances in computational techniques and hardware, recognition of the particle-reactive behavior of many organic and inorganic pollutants, and the introduction of new treatment technologies have indicated the critical role that interfacial phenomena play in the environment and in the technologies used to protect it. Advances in low Reynolds number hydrodynamics, new techniques for experimental surface analysis, the development of fractal mathematics, and the introduction of new and sensitive methods for measuring interparticle forces exemplify developments in colloid and surface chemistry that have present or potential application in the study of environmental interfaces.

Organic macromolecules are ubiquitous in aquatic systems. Research directions toward the conformations of these macromolecules within the interfacial region at the solid-liquid interface and the corresponding effects of these substances on a variety of reactions comprise the theme of this paper. Some examples of such reactions are: (i) natural coagulation and sedimentation in surface water, (ii) particle transport and deposition in ground waters, (iii) the fouling of microfiltration, ultrafiltration, and reverse osmosis membranes, (iv) microbial attachment, (v) oil-water separation, (vi) the effects of humic substances on the capacity and kinetics of activated carbon systems, and (vii) microflocculation by ozone.

This paper is written with four specific objectives:

1. to examine the structure of solid-liquid interfaces in aquatic systems, incorporating in this assessment the ubiquitous presence of organic macromolecules at these interfaces;
2. to identify some present difficulties in understanding and characterizing solid-water interfaces in environmental processes;
3. to outline a framework for modeling these interfacial regions with emphasis placed on colloidal stability, particle-particle interactions, coagulation, and deposition; and
4. to speculate about the sensitivity of selected environmental systems to interfacial properties.

The Solid-Liquid Interface in Natural Systems

There is extensive evidence from fresh waters, estuaries, and the oceans that the surface properties and the colloidal stability of particles in natural waters are affected by naturally occurring organic substances dissolved in these waters. These effects of natural organic matter (NOM) in establishing colloidal stability are also expected to occur in subsurface environments and to affect the passage/retention of pollutants in ground water aquifers.

The predominant fraction of NOM in natural waters is comprised of humic substances. These are anionic polyelectrolytes of low to moderate molecular weight; they have both aromatic and aliphatic components and can be surface active; they are refractive and some can persist for centuries or longer; they are produced by biological processes and are present to some extent in all natural waters. They adsorb on most surfaces and impart stability to particles in aquatic systems. Some investigators have observed that major divalent metal ions in natural waters (in particular, Ca^{2+}) can exert destabilizing effects on natural and synthetic particles at low to moderate metal ion concentrations. A consequence of these observations is that particles and associated particle-reactive pollutants may be expected to remain stable in soft waters that are high in NOM; in such waters they will remain in suspension in lakes and travel long distances in aquifers. When particles are present in hard waters that are low in NOM, they may be expected to be unstable and to be deposited in lake sediments and aquifers, retaining particle-reactive pollutants in bottom sediments and clogging aquifers. The consequences of colloidal stability on environmental quality can be diverse and substantial.

The effects of humic substances and divalent metal ions on the colloidal stability of natural particles are common observations without clear origins. Early studies showed that particles carry a negative charge in the presence of natural organic matter, regardless of the composition of the solid phase. This was taken as indirect evidence that humic substances stabilize particles electrostatically; calcium ions, in turn, might contribute electrostatically to particle destabilization. More recently, there has been speculation that nonelectrostatic (steric) effects are involved in the stabilization of particles by humic materials and that specific chemical interactions (complex formation) are involved in colloid destabilization by divalent metal ions. There is, however, no conclusive evidence, and a consistent theory to support these hypotheses has not yet been developed. Some speculations follow.

A consideration of the interaction between two suspended particles (e.g., in a lake) or between a suspended particle and a stationary collector (e.g., in a ground water aquifer) can begin with a determination of the structure of a single solid-solution interface. With this established, the interaction between two solid bodies (as characterized by force, free energy, or disjoining pressure) can be addressed.

The magnitudes of the interaction forces that determine stability in particle-particle interactions depend on the properties of each solid-solution interface. Electrostatic forces are almost universal in water since few particles are uncharged in aquatic environments, at least over a substantial pH range. Electrolytes and pH strongly affect the magnitude of these electrostatic forces. Specific chemical interactions between solutes and surfaces can be decisive in establishing surface properties and structure. Steric effects are potentially most significant in systems containing uncharged particles with adsorbed nonionic macromolecules. In this case, the amount of adsorbed polymer and solvent quality are important factors. The relative importance of electrostatic and steric effects is not clear in systems containing charged surfaces and adsorbed macromolecules, especially if the macromolecules are ionizable.

The Solid-Solution Interface and Colloidal Stability

There are two potential contributions to the structure of a solid/solution interface: (1) an electric double layer (termed EDL) and (2) a macromolecular adsorbed layer (denoted here as MAL). Separately these two structures are understood fairly well, at least in simplified cases. However, less is known about the effects of charge in the EDL on the conformation of adsorbed macromolecules in the MAL and, reciprocally, about the effects of charged and uncharged macromolecules on EDL properties. A schematic representation of such an interface is presented in Figure 1 (adapted from Lyklema, 1976) and discussed subsequently in this paper.

These two distinct contributions result in two distinct mechanisms for colloidal stability termed *electrostatic* and *steric* stabilization. Electrostatic stabilization results from energetically unfavorable overlap of the diffuse ion atmospheres surrounding all charged particles in water. The well known Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Verwey and Overbeek, 1948) of the electrical double layer and colloidal stability provides a model for evaluation of the combined effects of electrostatic repulsion and van der Walls attraction between surfaces in the absence of adsorbed macromolecules and when all chemicals can be treated as point charges. When electrostatic repulsion dominates over van der Waals attraction, the results are termed "slow" coagulation and "unfavorable" deposition and filtration. A good didactic summary has been given by Lyklema (1978).

Steric stabilization can result from the adsorption of polymers at solid-water interfaces. Large polymers can form adsorbed segments on a solid surface with loops and tails extending into solution (Figure 1 and Lyklema, 1978). Steric stabilization results from energetically unfavorable intermolecular interactions and entropically unfavorable compression in overlapping macromolecular adsorbed layers. Steric effects are likely

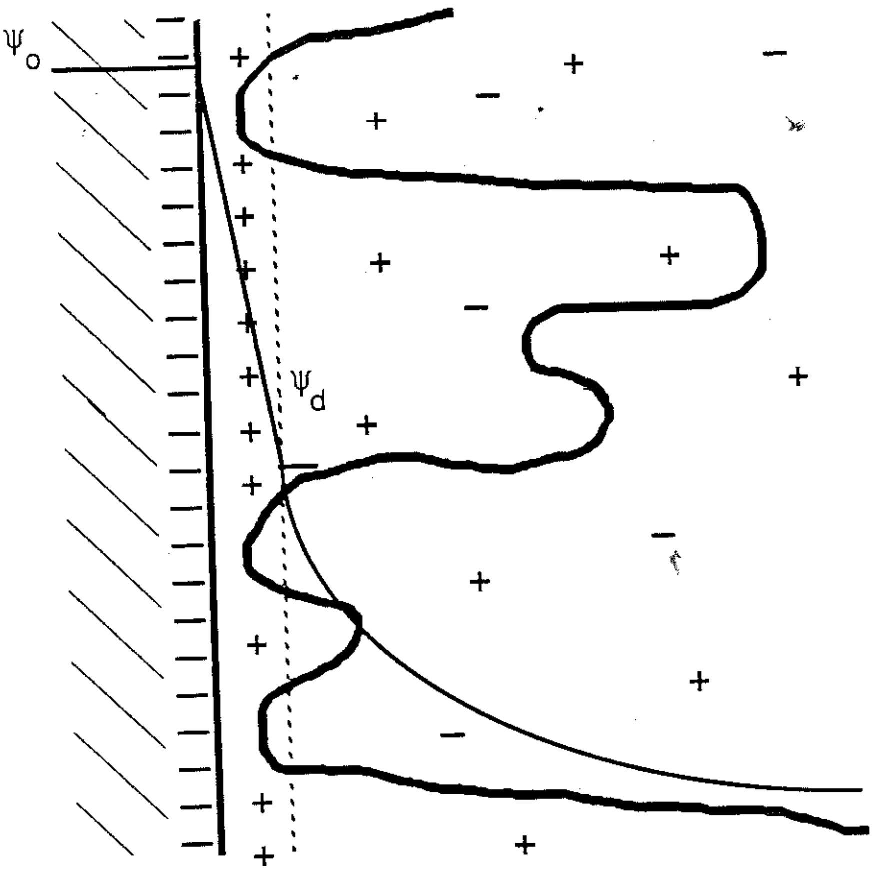

Figure 1. Schematic picture of a macromolecular adsorbed layer (MAL) and the electric double layer (EDL), after Lyklema (1976).

to be important when the thickness of the macromolecular adsorbed layer is about the same or larger than the diffuse layer thickness. In the absence of charge effects, the energy of interaction between the adsorbed layers on two particles can be calculated by summing the various contributions to the free energy of the system as a function of the distance separating the surfaces. Under conditions of unfavorable intermolecular interactions, a repulsive interaction energy develops when the particles are close enough so that dangling tails (Figure 1) of adsorbed macromolecules interact. On close approach, conformational entropy losses can give rise to strong repulsion if desorption of the macromolecules does not occur. When surface coverage is incomplete so that open sites remain available for adsorption, dangling tails can adsorb to the opposite surface, leading to aggregation.

In considering the conformation of macromolecules at interfaces, a segment can be operationally defined as a small portion of a macromolecule that can be considered as a single unit in terms of both functionality and flexibility (e.g., a monomeric unit in a polymer). The most important structural characteristics of the MAL are the segment density distribution near the surface and the conformations of the adsorbed molecules. The conformation of a flexible linear molecule adsorbed at an interface is described in terms of adsorbed trains, extended loops, and up to two extended tails. The equilibrium adsorbed state is determined by a balance of conformational entropy losses, intermolecular interactions, and surface-solute interactions. The surface/solvent/macromolecule interactions may be specific, hydrophobic, or electrostatic in origin (Westall, 1987). Specific interactions include van der Waals forces, hydrogen bond formation, and chemical reactions such as complexation and ligand exchange.

Polymer adsorption has been the subject of extensive experimental and theoretical investigations. The first stochastic model of polymer adsorption was developed in 1953 (Simha et al., 1953). Currently, several advanced models of polymer and polyelectrolyte adsorption are based on the work of Scheutjens and Fleer (1979, 1980; termed here the SF theory). Recent reviews of polymer adsorption include publications by Vincent and Whittington (1982) and Fleer and Lyklema (1983); the adsorption of polyelectrolytes is discussed by Hesselink (1983).

SF theory is a statistical thermodynamic model in which chain conformations are formulated as step-weighted random walks on a lattice. The simplified problem involves the adsorption of flexible linear homodisperse polymers comprised of identical uncharged segments at a uniform planar surface. Interactions among surface, adsorbate, and solvent are quantified using adjustable composite parameters; mechanistic details are neglected. The equilibrium MAL is determined by minimizing the total free energy of the system. That is, the canonical partition function is maximized with respect to the number of chains in each possible configuration, allowing specification of the distribution of chains, loops, and tails in the interfacial region.

In general, SF theory predicts an exponential decay in the segment density distribution close to a surface. At greater distances, tails dominate the segment density and the decay with distance is much less. For moderately sized polymers, a typical root-mean-square adsorbed layer thickness is 5 to 10 nm. Tails may extend as far as 20 nm, and may have a significant influence in particle-particle interactions. The extent of adsorption increases with the molecular weight and concentration of the polymer, with surface affinity, and with decreasing solvent quality.

The effects of polymer dispersivity were considered by Cohen Stuart et al. (1980). High molecular weight polymers adsorb preferentially to smaller ones at equilibrium, due to their smaller conformational entropy loss on adsorption and their greater opportunities to form favorable contacts with the surface. However, small polymers may adsorb preferentially compared with large ones at short times due to their faster rate of molecular diffusion to the particle surface.

SF theory has been extended to polyelectrolytes (van der Schee and Lyklema, 1984; Papenhuijzen et al., 1985; Evers et al., 1986). Because of intermolecular electrostatic repulsion, polyelectrolytes adsorb in flat conformations. With increasing electrolyte concentration, polyelectrolytes behave more like uncharged polymers and adsorption can increase with increasing ionic strength. Because polymer and surface charge are usually dependent on pH, adsorption is a strong function of pH.

Uncharged macromolecules have significant effects on the properties of the electric double layer. For example, potentiometric titration of a silver iodide - polyvinyl alcohol (PVA) system showed a decrease in the slope of the curve of surface charge versus pAg with increasing amount of PVA adsorbed, as well as a shift in the point of zero charge (p.z.c.) to smaller pAg (Koopal and Lyklema, 1975). The reduction in slope indicated a decrease in the differential capacitance; the shift in the p.z.c. indicated change in the surface potential. In interpreting these observations, a useful approximation is to consider train segments of the polymer to be located in the Stern layer, and loop and tail segments to be in the diffuse layer (Figure 1 and Lyklema, 1976). The dimension of a polymer segment is of the order of 0.5 nm, and train segments displace specifically adsorbing ions and water molecules. Loop and tail segments displace ions and water molecules in the diffuse layer. Possible consequences include:

- Reduction of the differential capacitance in the Stern layer due to displacement of specifically adsorbing ions or to a reduction in the dielectric constant.
- Change in the surface potential due to replacement of water dipoles by nonpolar polymer segments.
- Change in local activity coefficients.
- Outward shift of the plane of electrokinetic shear.
- Expansion of the diffuse layer.
- Binding of water molecules in the diffuse layer of hydrophilic polymer groups, reducing the local dissolving power of water (Derjaguin et al., 1987).

Charged macromolecular species have even more complex effects on EDL properties than do uncharged polymers. Ionized macromolecular segments contribute fixed charge in the diffuse layer as well as in the Stern layer, so that the local distribution of mobile indifferent electrolytes is affected. The conformation of the adsorbed polyelectrolytes (the distribution of charged segments in the EDL) is also dependent on the local electrolyte concentration. Finally, specific interactions between small ions (e.g., Ca^{2+}) and macromolecular functional groups (e.g., carboxyl and phenolic groups in humic substances) may also alter the charge and conformation of the macromolecular groups.

London-van der Waals forces arise from random density variations in the electron clouds of atoms that provide a fluctuating electromagnetic field. Hamaker (1937) developed an expression for the energy of interaction between two macroscopic bodies by assuming pair-wise additivity of the van der Waals interaction energies between constituent atoms or molecules. This approach is still commonly used despite the development of a more detailed (and more cumbersome) treatment by Lifshitz and coworkers (Gregory, 1986).

The presence of dense macromolecular adsorbed layers can significantly affect the van der Waals interaction between two particles. Usually, the result is to increase the attraction (Vincent, 1974). An approximation can be made to correct the Hamaker expression by treating the particles as composites consisting of the solid plus the adsorbed layer (Vold, 1961). Thus, the pair-wise addition of interaction energies can be computed using two Hamaker constants for each composite particle, one for the underlying solid and one for the adsorbed layer.

Although MAL interactions are usually modeled using thermodynamic concepts, the dynamics of the particle-particle encounter can be important in determining the outcome (Lyklema, 1985). As two particles approach each other, the rising local polymer concentration between the particles becomes a driving force for polymer desorption. If the rate of desorption and diffusion of the polymers is fast compared to the rate at which the particles approach each other, full equilibrium is maintained and polymer desorption occurs. In the absence of an electrostatic energy barrier, full equilibrium would inevitably result in aggregation due to van der Waals attraction; the intervening polymers would simply desorb and diffuse away. However, full equilibrium is unlikely to occur in most systems since the kinetics of polymer desorption and polymer diffusion are typically very slow. A more realistic assumption for most particle-particle interactions is restricted equilibrium, where the rate of polymer desorption is slow and the rate of conformation adjustment is fast. In this case, the total amount of adsorbed polymer remains constant as particles approach and interact. An energy minimum may or may not result at some intermediate separating distance, depending on whether intermolecular interactions are favorable or unfavorable. The dynamics in actual particle-particle interactions are expected to lie between these two extreme cases.

The energy of interaction between two adsorbed layers can be calculated by summing the various contributions to the free energy of the system as a function of the distance separating two surfaces. An advanced statistical model of interacting adsorbed polymer layers using a lattice configuration in the interfacial region has been developed by Scheutjens and Fleer (1985). This model is based on SF theory for polymer adsorption at a single interface, modified by the addition of a second boundary. At any given separation distance, the complete equilibrium segment density distribution and the contributions of trains, loops, tails, and bridges can be computed. The assumption of either full or restricted equilibrium during a particle-particle encounter is included as a boundary condition.

Using the SF model and assuming restricted equilibrium, no bridging, and unfavorable intermolecular interactions, there is no effect on the particles until they approach close enough for the dangling tails of adsorbed molecules to begin to interact. A small repulsive energy is developed which increases slowly as the particles approach more closely. When the local macromolecular concentration is high enough that molecular conformations are significantly restricted, the repulsive interaction increases very rapidly as the separating distance narrows. In the absence of bridging or a DLVO type of energy minimum, aggregation is prevented. The particles are sterically stable.

Research to apply these concepts to natural aquatic systems could have three components: (1) model development of the interfacial region for a system comprised of charged particles, adsorbed anionic macromolecules (MAL), and inorganic ions (EDL), (2) experiments involving model and natural colloidal particles, model and natural aquatic organic substances, and inorganic solutions with compositions representative of fresh waters including a range of pH and divalent metal ion concentration, and (3) applications to environmental problems in surface waters, ground water aquifers, and treatment systems. A possible modeling framework follows.

Modeling Framework

Chemical modeling of aquatic systems can be done in a variety of ways. In this paper, chemicals are classified into three types to provide a framework for thought, discussion, experimentation, and modeling. These types are (i) mathematical chemicals, (ii) model chemicals, and (iii) aquatic chemicals.

Mathematical Chemicals

A variety of chemicals used in modeling aquatic systems do not exist in physical form. Examples include the point charges in the Debye-Huckel theory for activity coefficients of ions in solution, the Gouy-Chapman model for the electrical double layer, the DLVO theory for particle-particle interactions and colloidal stability, and the linear, flexible macromolecules used by Scheutjens and Fleer in describing the conformations of macromolecules at interfaces and the interactions between two MALs in colloidal stability. Such chemicals are termed mathematical or imaginary in this paper.

These mathematical chemicals have been used with great vigor and substantial success in describing and understanding several phenomena in aquatic systems, but they have some severe limitations. They are chemicals without a chemistry, i.e., they do not represent the specific chemical reactivity of real atoms, ions, or molecules. They exist only in the mind of the chemist who uses them in modeling. The DLVO model, for example, has described the effects of charge on the concentration of simple solutes required to coagulate many suspensions (the Schulze-Hardy rule), but it has been unsuccessful in describing the effects of particle or solution properties on coagulation kinetics. This severely restricts its use in natural or engineered systems where rate processes are often the principal interest. It is likely that substantial new understandings about interfacial phenomena will not result from further mathematical development of the mathematical chemicals in the DLVO theory; it is more likely that this approach will be used in some applications as one component of models which incorporate other reactions, often chemical in origin.

As indicated previously in this paper, mathematical chemicals are being widely used at present in describing the properties of macromolecules at interfaces (the MAL) and in modeling the interactions between two solid-water interfaces with MALs (e.g., SF theory). Considerable further work in this area is warranted. The conformation of polymers and polyelectrolytes at charged interfaces, the effects of the EDL on an MAL and the accompanying effects of an MAL on the EDL (e.g., Figure 1), and the interactions between two such interfacial regions are questions for which answers can be provided at least partly, albeit not completely, by mathematical modeling with appropriate mathematical chemicals. The results can have use in such processes as membrane fouling, carbon adsorption, coagulation with synthetic organic polyelectrolytes and polymers, and solid-water separation processes in natural and engineered systems.

Model Chemicals

Model chemicals are authentic chemicals, but they are models of natural systems, not replicas of them. They have been used to test some theories and to develop others; their use in modeling natural systems has been extensive and valuable. As considered here, model chemicals can be used in well-defined laboratory experiments and also in mathematical models but are often not significant themselves in natural or engineered systems. Examples include silver halide sols in studies of colloidal stability, mercury drops in polarographic experiments, octanol as used to characterize solid-water partitioning of hydrophobic organic compounds, and diverse organic and inorganic complexing agents used in experimental and mathematical studies of metal speciation.

These model chemicals exist and have individual and specific chemical properties. They are selected to represent significant characteristics of aquatic systems and to add important chemical properties and reactions to models that may also include mathematical chemicals. They may be used, for example, in complex mathematical models such as MINEQL and others to characterize speciation in aquatic systems at equilibrium. They may be assigned mathematical properties such as charge or segment length, but each is distinguished from all others by specific chemical properties.

Experiments using model chemicals in laboratory studies are essential for understanding and modeling chemical phenomena in aquatic systems. They have been used with great success but, as with mathematical chemicals, they have significant limitations. Their selection and appropriate use forms much of the art of research in aquatic chemistry. This is especially true in kinetic studies. Extensive laboratory research is presently being conducted using model chemicals to study the kinetics and mechanics of such interfacial processes as chemical weathering, iron cycling in lakes, and abiotic redox reactions involving synthetic organic pollutants.

Appropriate model chemicals for studying the kinetics of colloidal stability of natural particles in aquatic systems are difficult to determine. The classic silver halide sols do not have chemical properties that are pertinent to aquatic systems. Latex particles, often used because of their physical properties (size and density), require careful attention to their surface chemistry. For example, many of the surfactant-free lattices exhibit hydrophobic characteristics at low ionic strengths. The ubiquitous presence of natural organic substances in aquatic systems, as stated previously, exerts substantial effects on colloidal stability and may dominate membrane fouling, but the model chemicals appropriate for studies of the effects of NOM on these phenomena remain to be established.

It is probable that a variety of model chemicals will be needed in laboratory studies and in models to characterize the interfacial region and its effects on particle-particle interactions in natural aquatic systems. Suitable solid surfaces could include metal oxides such as SiO_2, Al_2O_3, MnO_2, TiO_2, and Fe_2O_3, latex particles with a variety of functional groups and hydrophobicity, hydrophobic solids, and perhaps bacteria with defined and reproducible surface characteristics. Model chemicals for the inorganic solutes in natural waters are more easily selected; pH, major divalent cations such as Ca^{2+}, and ionic strength are easily identified. Problems arise with chemical models for natural organic matter. Simple monomeric solutes such as salicylic acid can simulate the interaction of the functional groups on macromolecules with solid surfaces, but they cannot serve as surrogates for the conformation of macromolecules in and beyond the diffuse layer or for many interactive effects between an MAL and the EDL. Linear, flexible polymers and polyelectrolytes such as polyethylene oxide, polystyrene sulfonic acid, and polyacrylic acid are more suitable; they should have defined molecular weights with narrow distributions. Model proteins may be needed to represent those proteins that actually gain entropy on adsorption due to an increase in conformational entropy as intramolecular bonds in helical structures are broken. This latter process may be important in the slow fouling of ultrafiltration membranes as high molecular weight substances preferentially accumulate at membrane surfaces from very low concentrations over extended time periods.

Aquatic Chemicals

As considered here, aquatic chemicals are those that exist in natural and engineered aquatic systems. Some, such as Na^+, are characterizable with some rigor; others such as iron species are not. While these chemicals exist in the real world outside of the mind of the chemist, many of them may not be identifiable chemically. For example, iron in a lake may be particulate or dissolved (a distinction that has operational properties and may itself not be definitive); it may be oxidized or reduced [Fe(III)] or [Fe(II)], present as hydroxo or other inorganic complexes, be monomeric or in polymeric form, and be present in many organic complexes. Aquatic chemicals, then, are often not defined or definable with rigor.

Evaluating colloidal stability and its effects in natural systems requires measurements in natural systems. Inputs are required for water quality models and they are generally lacking in studies of particulate processes in aquatic systems. Allochthonous inputs are rarely known in surface waters and are essentially unknown in ground water aquifers. The biotic and abiotic processes leading to the formation and destruction of particles in aquatic systems are not described in form or with sufficient quantitative rigor to provide accurate information of these input and loss reactions. Some information about the responses of aquatic systems is being developed, both in surface and subsurface environments. Particle deposition in sediment traps in lakes, particle concentrations and size distributions in surface waters, and particle characteristics in ground waters are being reported to a limited but increasing extent. Models to relate inputs and outputs, or causes and effects, are being developed. They are limited, in the judgment of the writer, primarily by a lack of chemical information about the solids, the solutions, and the interfacial regions in these systems, coupled with uncertainty about system inputs.

Finally, effective modeling of the chemistry of particle-particle interactions in natural aquatic systems requires the use of all of these types of chemicals: mathematical, model, and aquatic; with the appropriate mix probably depending on the problem to be addressed.

Some Environmental Systems

Some speculations about the role of interfacial regions in three environmental systems follow. The three areas, selected to be illustrative but not comprehensive, are (i) the transport of particles in ground water aquifers, (ii) the coagulation and sedimentation of particles in lakes, and (iii) the effects of ozone as a microcoagulant in water treatment.

Particle Passage/Retention in Ground Waters

When colloidal particles are stable, i.e., when they do not aggregate readily or adhere to surfaces, they may be expected to travel long distances in ground water systems and to carry particle-reactive pollutants with them. When they are unstable, i.e., when they aggregate rapidly or attach to solid surfaces, they can be expected to deposit extensively in porous media and to reduce aquifer permeability. Both types of behavior have been observed. It is proposed here that one important key in this problem is the chemistry of the solid-solution interface and, in turn, that the chemistry of the interfacial region is often controlled by the composition of the aqueous phase in natural systems and at hazardous waste sites.

As stated previously, natural organic compounds have a dramatic impact on colloidal stability. Dissolved natural organic matter stabilizes particles and retards aggregation, deposition, and filtration processes. The metabolic activity of microbes markedly influences the composition and concentration of organic matter in aquatic environments. Consequently, microbial exudates are a source of stabilizing macromolecules that can coat particles and affect particle dynamics. Characterization of this material and its impact on particle-particle interactions is important to predicting the transport and fate of particles in natural environments and in solid-liquid separation technologies.

Microorganisms behave as particles in response to external forces and, if they do not aggregate or adhere to surfaces, they may be expected to travel long distances in ground water systems. Movement of pathogenic bacteria, protozoa, and virus is of particular concern because their presence in ground water used for drinking poses a potential health hazard. Two major factors control fate: survival and migration. The longer a pathogen persists, the greater the chance that it will be capable of causing infection after transport. Improved knowledge of particle-particle interactions provides a base for addressing the issue of microbial transport. Chemical aspects play a strong role in the stability of particles and microorganisms. When chemical effects can be neglected and the interaction between pathogens and surfaces is favorable, present physical transport models (e.g., Tobiason and O'Melia, in press) are likely to predict the kinetics of deposition. When chemical effects are important, all experimental results indicate that the chemical aspects of particle-particle interactions are very poorly understood (e.g., O'Melia, 1987). Observed rates of coagulation, deposition, and filtration are substantially less than in favorable cases, but are many orders of magnitude greater than any theoretical predictions. These results suggest that pathogens could remain in suspension in ground waters that are high in dissolved organic carbon (DOC) and low in hardness. Greater deposition is likely to occur in hard ground waters with low DOC. Improvements in theory and measurements of particle-particle interactions under subsurface conditions are needed for better quantitative predictions. This information is potentially useful for placement and development of attached bacteria in the subsurface to maximize interaction with organic contaminants during in situ biorestoration. Deposition of biomass can also alter the permeability of an aquifer.

Research into the characteristics of microbial interfaces and of the reactions occurring at the microbe-solution interface will have impact on our understanding of biogeochemical processes, on our ability to protect the public health, on implementation of developments in biotechnology, on the development of processes for the biodegradation of synthetic organic pollutants, on our ability to forecast the fate of most pollutants in the environment, and on many other environmental problems.

Coagulation in Lakes

Coagulation occurs in all natural waters, although its significance can vary widely. Weilenmann (1986) has applied coagulation modeling to Swiss hardwater lakes. One effect of coagulation in lakes is to increase settling velocities of particles by aggregation, thereby reducing their residence time in the water column and increasing the flux of particles and particle-reactive substances to the sediments. A second process in hardwater lakes is mutual coagulation of dense $CaCO_3$ with algae, leading to an increase in the sedimentation rates of organic biomass in aggregates with a bulk density greater than that of the free microorganisms.

It is customary and convenient to describe the colloidal stability of particles in an aqueous suspension by a sticking or stability factor, α, defined as follows:

$$\alpha = \frac{\text{interparticle attachment rate}}{\text{interparticle collision rate}}$$

The sticking or stability factor is thus the ratio of the collision rate producing aggregates to the total rate at which collisions occur by such physical processes as Brownian motion, fluid shear, and differential sedimentation (e.g., O'Melia, 1987). For a perfectly stable suspension, all physical collisions are unsuccessful and $\alpha = 0$. For a completely destabilized or sticky suspension, all collisions produce aggregation and $\alpha = 1$.

Experimentally measured particle stability coefficients (α) for fresh surface waters range over two orders of magnitude, from about 0.001 to more than 0.1, and support the view that solution chemistry can control the colloidal stability of natural particles in aquatic systems. Major divalent cations such as Ca^{2+} destabilize particles (increase α) and dissolved NOM stabilizes them (decreases α). Since solution chemistry varies widely among lakes, it is expected and observed that stability or sticking factors vary accordingly. In turn, the importance of coagulation as a process in lacustrine systems is expected to depend on solution chemistry, with low aggregation rates in soft colored waters and rapid coagulation occurring in hard waters that are low in NOM. Field observations of Lakes Zurich and Sempach support this view (Weilenmann, 1986).

Research into the origins of the stability of particles in natural waters and the mechanisms by which particle stability is affected by solution chemistry in natural systems will yield new knowledge about the speciation and conformation of solid-solution interfaces in natural waters, provide understanding of the forces involved in particle-particle interactions in natural systems, and enhance predictive capability for the transport and fate of particle and particle-reactive pollutants in both surface waters and subsurface environments.

Ozone and Microcoagulation

Ozone has many uses in water treatment, including disinfection, oxidation, color removal, taste and odor control, and enhancement of biological activity in activated carbon systems. It has also been found under some but not all circumstances to destabilize natural particles and act as a coagulant. This latter effect is observable but not predictable. Some reaction of ozone with NOM is usually suggested, although proposals range from the polymerization of low molecular weight humic substances to form high molecular weight materials that act as bridges between particles to the oxidation of adsorbed humic substances to form smaller compounds that desorb and thereby leave the particles more sticky or unstable.

Some definitive experiments have been conducted by Dowbiggen (1986). The kinetics of the coagulation of suspensions of Al_2O_3 were determined in solutions containing varying concentrations of aquatic fulvic acid and Ca^{2+}; some suspensions were treated with varying doses of ozone. The results indicated that low concentrations of fulvic acid (less than 1 mg/L) retarded the aggregation rate of Al_2O_3 and that relatively low concentrations of Ca^{2+} reduced or eliminated this effect. Such observations are consistent with previous studies. When ozone was applied to suspensions containing Al_2O_3 and fulvic acid but no Ca^{2+}, the kinetics of coagulation remained unchanged. The particles were stabilized by fulvic acid and this stability was not altered by the addition of ozone. In contrast, when ozone was applied to suspensions containing Al_2O_3, fulvic acid, and Ca^{2+}, coagulation kinetics increased substantially (α increased) to a considerably greater extent than observed for Ca^{2+} without ozone addition. While these results provide a framework for testing the potential effectiveness of ozone as a coagulant (it might be useful for inorganic particles in hard waters but not in soft ones), the effect lacks a mechanistic interpretation. A preliminary, simplistic, and speculative hypothesis follows, presented here to illustrate the complexity of the solid-water interface in natural systems.

Consideration of the mode of action of ozone as a coagulant can begin with a consideration of the origins of the stability of particles in natural systems. The ionic strength of fresh waters may vary from about 10^{-4} to

10^{-2}, with corresponding diffuse layer thicknesses (Figure 1) ranging from 30 to 3 nm. Aquatic humic substances range in molecular weight from about 500 to perhaps 50,000 daltons, so that the dimensions of the EDL and the MAL can be comparable in many natural systems. This indicates that the colloidal stability of particles in fresh water environments can be affected by the chemistry of both small, primarily inorganic solutes and larger natural macromolecules, and that the interactions between these groups of species can be important in determining stability in natural systems. At low ionic strength and in the absence of Ca^{2+}, the charge on anionic humic substances could stretch these molecules and cause them to adsorb in a flat configuration, limiting both the amount of organic matter adsorbed and the distance to which it extends from the surface into and through the diffuse layer (which would be about 30 nm in thickness). Under these circumstances the thicker EDL could dominate particle stability. At higher ionic strength in a fresh water (ca. 10^{-3}), humic substances could coil partially, adsorb more extensively, and also extend into the diffuse layer which would have a thickness of about 10 nm. These fixed charges in the diffuse layer would contribute to electrostatic stabilization, but not in a manner described by conventional EDL mathematics. Some steric effects might also occur. At higher ionic strength (ca. 10^{-2}), the thickness of the EDL (ca. 3 nm) could be less than the MAL, so that the charge and configuration of the adsorbed organic macromolecules could control particle stability. Divalent metal ions such as Ca^{2+} can react specifically with functional groups on humic substances, altering macromolecular conformations in the MAL, increasing adsorption, and probably also reducing both the charge and the thickness of the MAL. Both effects would reduce colloidal stability (increase α) and lead to enhanced rates of coagulation and deposition.

Ozonation might perturb this picture, probably by reacting with natural organic matter as proposed by others. It may not be necessary, however, either to polymerize the humic substances or to fractionate them into smatter molecules that desorb. Reactions that produce functional groups on the humic molecule that can then complex with Ca^{2+} could destabilize particulate materials by increasing calcium effects on the conformation and net charge of the organic molecules in the MAL.

It is important to note here that this treatment of ozone as a microcoagulant is completely speculative and needs extensive additional theoretical and experimental examination.

Concluding Remarks

Until the 1950s, research and applications in environmental protection were directed at microbial pathogens and at managing oxygen resources in natural waters by oxidizing degradable organic matter in biological treatment plants. In the 1960s, attention was directed at soluble nutrients such as phosphorus and nitrogen and their impact on cultural eutrophication. The present focus in protecting the environment is on substances that, in general, attempt to leave the aqueous phase by partitioning into the atmosphere or to solid phases. PCBs in the Great Lakes are volatile, partition into the tissues of fish, and deposit in lake sediments. Carbon dioxide is injected into the atmosphere by fossil fuel combustion and must eventually be transported to ocean sediments as particulate $CaCO_3$. Solvents buried in hazardous waste sites are prevented from volatilizing to the atmosphere and so will partition there into organic particles or be transported in reluctant solution in ground water aquifers. The herbicides and pesticides released to the Rhine River by the Sandoz accident in Basel, Switzerland were particle-reactive, accumulated in sediments of the Rhine, and had their greatest impact on benthic organisms. Radionuclides released by the Chernoble accident were transported atmospherically, collected by rainfall and fog, and accumulated as dry deposition on plant surfaces. This event as well as any other exemplifies the coupling of the atmospheric, aquatic, and terrestrial conveyor belts that exists in the global environment, and the significance of particles and interfaces in environmental processes.

> "One of the greatest future tasks of environmental engineers and scientists is to understand the nature of interfaces and the processes that occur at the surfaces. Significant progress is possible both in technological processes, e.g., in water and wastewater treatment, as well as in quantifying transfer and cycling processes. Evidently, environmental changes involve complex interactions between the inorganic physical processes and the biological processes that occur at the microlevel at interfaces, and they influence the macrosystems." (Stumm, 1988)

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References

Cohon Stuart, M.A., Scheutjens, J.M.H.M., and Fleer, G.J. (1980), "Polydispersivity Effects and the Interpretation of Polymer Adsorption Isotherms," *Journal of Polymer Science: Polymer Physics Edition, 18*, 559-573.

Derjaguin, B.V., Dukhin, S.S., and Yaroshchuk, A.E. (1987), "On the Role of the Electrostatic Factor in Stabilization of Dispersions Protected by Adsorption Layers of Polymers," *Journal of Colloid and Interface Science, 115*, 234-239.

Dowbiggen, W.B. (1986), "Factors Affecting the Stability of Particles in Natural Waters and Their Susceptibility to Ozone-Induced Microflocculation," unpublished masters report, University of North Carolina, Chapel Hill.

Evers, O.A., Fleer, G.J., Scheutjens, J.M.H.M., and Lyklema, J. (1986), "Adsorption of Weak Polyelectrolytes from Aqueous Solution," *Journal of Colloid and Interface Science, 111*, 446-454.

Fleer, G.J. and Lyklema, J. (1983), "Adsorption of Polymers," in G.D. Parfitt and C.H. Rochester, Eds., *Adsorption from Solution at the Solid/Liquid Interface*, Academic Press, London.

Gregory, J. (1986), "Colloid Interactions," paper presented at IXth European Chemistry of Interfaces Conference, Zakopane, Poland, May 19-24.

Hesselink, F. Th. (1983), "Adsorption of Polyelectrolytes from Dilute Solutions," in G.D. Parfitt and C.H. Rochester, Eds., *Adsorption from Solution at the Solid/Liquid Interface*, Academic Press, London.

Koopal, L.K. and Lyklema, J. (1975), "Characterization of Polymers in the Adsorbed State by Double Layer Measurements. The Silver Iodide + Poly(vinylalcohol) System," *Discussions of the Faraday Society, 59*, 230-241.

Lyklema, J. (1976), "Inference of Polymer Adsorption from Electrical Double Layer Measurements," *Pure and Applied Chemistry*, *46*, 149-156.

Lyklema, J. (1978), "Surface Chemistry of Colloids in Connection with Stability," in K.J. Ives, Ed., *The Scientific Basis of Flocculation*, Sitjhoff and Noordhoff, The Netherlands, 3-36.

Lyklema, J. (1985), "How Polymers Adsorb and Affect Colloid Stability," in B.M. Moudgil and P. Somasundaran, Eds., Proceedings of the Engineering Foundation Conference, Sea Island, Georgia, Jan 26-Feb 1.

O'Melia, C.R. (1987), "Particle-Particle Interactions," in W. Stumm, Ed., *Aquatic Surface Chemistry: Chemical Processes at the Particle-Water Interface*, Wiley-Interscience, New York.

Papenhuijzen, J., van der Schee, H.A., and Fleer, G.J. (1985), "Polyelectrolyte Adsorption. I. A New Lattice Theory," *Journal of Colloid and Interface Science*, *104*, 540-552.

Scheutjens, J.M.H.M. and Fleer, G.J. (1979), "Statistical Theory of the Adsorption of Interacting Chain Molecules. 1. Partition Function, Segment Density Distribution, and Adsorption Isotherms," *The Journal of Physical Chemistry*, *83*, 1619-1635.

Scheutjens, J.M.H.M. and Fleer, G.J. (1980), "Statistical Theory of the Adsorption of Interacting Chain Molecules. 2. Train, Loop, and Tail Size Distribution," *The Journal of Physical Chemistry*, *84*, 178-190.

Scheutjens, J.M.H.M. and Fleer, G.J. (1985), "Interactions between Two Adsorbed Polymer Layers," *Macromolecules*, *18*, 1882-1900.

Simha, R., Frisch, H.L., and Eirich, F.R. (1953), "The Adsorption of Flexible Molecules," *The Journal of Physical Chemistry*, *57*, 584-589.

Stumm, W. (1988), personal communication.

Tobiason, J.E. and O'Melia, C.R. (in press), "Physicochemical Aspects of Particle Removal in Depth Filtration," *Journal American Water Works Association*.

van der Schee, H.A. and Lyklema, J. (1984), "A Lattice Theory of Polyelectrolyte Adsorption," *The Journal of Physical Chemistry*, *88*, 6661-6667.

Verwey, E.J.W. and Overbeek, J.Th.G. (1948), *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam.

Vincent, B. (1974), "The Effect of Adsorbed Polymers on Dispersion Stability," *Advances in Colloid and Interface Science*, *4*, 193-277.

Vincent, B., and Whittington, S.G. (1982), "Polymers at Interfaces and in Disperse Systems," *Colloids and Surfaces*, *12*, 1-117.

Vold, M.J. (1961), "The Effect of Adsorption on the van der Waals Interaction of Spherical Colloidal Particles," *Journal of Colloid and Interface Science*, *16*, 1-12.

Weilenmann, U. (1986), "The Role of Coagulation for the Removal of Particles by Sedimentation in Lakes," unpublished doctoral dissertation, Eidgenossischen Technishen Hochschulen, Zurich.

Westall, J.C. (1987), "Adsorption Mechanisms in Aquatic Surface Chemistry," in W. Stumm, Ed., *Aquatic Surface Chemistry: Chemical Processes at the Particle-Water Interface*, Wiley-Interscience, New York.

Discussion: Chemical Processes - Water

Steven J. Eisenreich
Department of Civil and Mineral Engineering
The University of Minnesota
Minneapolis, MN

Chemical Interactions with Natural Aquatic Particles

A fundamental paradigm driving our studies and understanding of trace metals (including radionuclides) and organic contaminants in marine and lacustrine environments is that chemical interactions at natural particle surfaces control their transport, fate and availability. That is, the production, interaction, settling, decomposition, and recycling of aquatic particles controls the residence time of particle-reactive chemical species in natural waters. Likewise in ground waters, interactions of chemical species with aquifer solid phases exerts substantial control on chemical transport and availability. Aquatic solute-particle interactions may be described by processes affecting particle-particle interactions (including nature of particle phase), sorbate-sorbent interactions, and sorbate-solvent-natural organic matter (NOM) interactions. Professor O'Melia in his lead paper has discussed the importance of particle-particle interactions, especially as affected by macromolecular interactions with aquatic particles. This paper will address the research needed to elucidate the speciation and physicochemical state controlling fate and biotic availability.

Particle-Particle Interactions

Natural water particles may be characterized as aggregates composed of inorganic and organic matter, negatively charged, porous, unstable, and largely covered by NOM (microbial populations and partially-degraded OM). To properly elucidate particle-particle interactions, the following research is needed: a) rates of particle aggregation and disaggregation as affected by solution and surface chemistry, and mixing; b) particle size and surface area distributions, especially in the colloidal (<1 µm) range; c) number, strength and identity of surface binding sites; d) aggregate porosity and pore sizes; e) fractional surface coverage with OM; f) source, settling and decomposition characteristics; g) colloid formation and transport in sediment porewaters and groundwaters.

Sorbate - Sorbent Interactions

The last two decades have seen the evolution of the surface complexation model in elucidating the interactions of trace metals and anions with well-characterized metal oxide phases. There is a significant need to further extend the surface complexation model to solute interactions with natural or pseudo-natural particles. In contrast, interactions of organic contaminants with aquatic particles has been largely based on empirical correlations of chemical removal from solution to aqueous solubility or octanol-water partition coefficient. In this context, the soprtion of organic chemicals to particles needs to be studied using well-characterized solids of synthetic and natural origin, and an understanding developed of their physical chemistry in dilute solution. The active paradigm describing trace metal and organic chemical uptake is the reversible sorptive reaction with the surface followed by diffusion into the NOM matrix at the surface and/or the slow diffusion into pore spaces of the particle aggregate as affected by sorption to internal surfaces. Slow kinetics of desorption (trace metals, radionuclides, organics) may result from the rate-limiting particle disaggregation step. Research needs in this area are: a) NOM binding to aquatic surfaces; b) surface coverage of natural particles by OM; c) bacterial contribution to surface chemistry of natural particles; d) effect of particle aggregation on the kinetics and equilibrium of surface complex formation and organic chemical partitioning; e) organic chemical partitioning to, or release from, natural particles undergoing decomposition; f) equilibrium vs. kinetic approach to organic chemical partitioning; g) particle-catalyzed and particle-inhibited surface chemistry; h) overall role of biota in scavenging trace metals and organic chemicals from water; and i) mixed solvent and NOM effects on the aqueous activity of organic chemicals.

Solute - Solvent - Natural Organic Matter Interactions

Trace metals form soluble complexes with dissolved ligands (inorganic and organic) in natural waters. This may either enhance or inhibit formation of surface complexes. Hydrophobic organic compounds are thought to associate with DOM and colloidal matter affecting their affinity to particles. Evidence suggests that organic chemical association with NOM and organic colloids inhibits sorption to aquatic particles and makes the HOC unavailable for biotic uptake. Colloid aggregation acts to form larger particles. There are few studies of the thermodynamics of HOC association with NOM, colloids and solvents under conditions typical of natural or contaminated systems. Possible mechanisms of association include partitioning hydrophobic interactions, kinetics of diffusion in internal pore spaces, and a change in the aqueous activity coefficient. Mixed solvent effects on both metal and HOC sorption need to be studied. Research needs in this area include: a) competition of solution and natural particle binding sites for trace metals; b) DOM - metal binding in marine and freshwater systems; c) speciation of metals at low concentrations in presence of NOM and other ligands; d) mixed solvent effects (groundwater) on the speciation and activity of organic contaminants; e) development of methodology to speciate metals and organic compounds at low concentrations in natural waters; f) availability of dissolved and "complexed" metals for biotic uptake; and g) availability of dissolved and "complexed" organic chemicals in surface waters, sediment porewaters, and groundwaters.

Short Reading List.

Eadie, B.J. and Robbins, J.A. "The Role of Particulate Matter in the Movement of Contaminants in the Great Lakes", In *Sources and Fates of Aquatic Pollutants*, R.A. Hites and S.J. Eisenreich (Eds.), Advances in Chem Series No. 216, American Chemical Society: Washington, D.C., Chapter 11, p. 319-364, 1987.

Honeyman, B.D.; Santschi, P.H. Metals in aquatic systems. *Environ. Sci. Tech.*, 1988, 22, 862-871.

Honeyman, B.D.; Adamson, A.W.; Murray, J.W. The nature of reactions on marine particle surfaces. *Applied Geochem.*, 1988, 3, 19-26. (Panel Rept. No. 2, CHEMRAWN IV)

Karickhoff, S. Pollutant sorption in aquatic systems. *J. Hyd. Div.* (ASCE), 1984, 110, 707-735.

Stumm, W. (Ed.). *Aquatic Surface Chemistry: Chemical Processes at the Particle-Water Interface*, John Wiley: New York, 1987.

Wu, S.C.; Gschwend, P.M. Sorption kinetics of hydrophobic organic compounds to natural sediments and soils. *Environ. Sci. Tech.*, 1986, 20, 717-725.

Wu, S.C.; Gschwend, P.M. Numerical modeling of sorption kinetics of organic compounds to soil and sediment particles. *Water Resources Res.*, 1988, 24, 1373-1383.

Summary Discussion - Chemical Processes

Philip C. Singer
Department of Environmental Science and Engineering
University of North Carolina
Chapel Hill, NC 27599-7400

Chemical Processes - Air

Hoffmann presented a comprehensive overview of issues and current research needs in atmospheric chemistry. The issues he discussed emanated from a recent NSF-sponsored workshop organized by the Chemistry Division which he participated in as a member of the sub-section dealing with atmospheric chemistry. The principal theme of his comments was the need for fundamental studies of chemical kinetics and the measurement of atmospheric species. In addition to the items presented as part of his written comments, Hoffmann also pointed to the need for fundamental research into chemical methods of control technology for atmospheric emissions. He closed with a discussion of the chemistry of stratospheric ozone depletion, as presented in Example 2 of his written comments, and noted that the recent field work in Antarctica has verified the results generated from fundamental kinetic studies, underscoring the value of such fundamental studies.

In his discussion, Jeffries selected several items from among the list of atmospheric chemistry research needs to relate to current environmental policy issues. The problems listed in his written comments range from the urban/regional scale to the global scale. He noted that in the air quality field, models have more than an integrative and scientific value; they are actually used by regulators to make decisions and to establish emission controls. As a result, since much of the chemical information needed in these models is unknown, the resultant uncertainty weakens the credibility of our air quality control predictions, thereby making the policy-makers nervous. He closed by noting that any progress we make in this area in the next five years will have a significant impact on environmental policy.

In the discussion from the floor, Hoffmann was asked if NSF was responsive to the research needs developed by the workshop. He answered that the goal of the workshop was to prepare a document for NSF that their upper management could use to appeal to Congress for a greater appropriation of research funds. This document was completed this past summer (1989) and we will have to wait and see how successful NSF is in obtaining their appropriation request.

A second question had to do with the degree of uncertainty in the chemistry area versus that present in meteorology. Demerjian indicated that while there is significant uncertainty in the meteorological models, meteorologists have an opportunity to test their models on a daily basis. Hoffmann noted that there are very few comprehensive data sets that can be used to test models that include transport and chemistry, noting that we are data-poor in this area. In general, the meteorological models and studies tend to be more integrative of principles and observations, while the chemical studies tend to be more isolated and tend to depend more on first principles.

There was some discussion also of the biogenic emissions of hydrocarbons and the role of methane in the upper atmosphere. Hoffmann noted that the important question is where does the methane come from? Jeffries pointed out that some scientists believe that biogenic emissions may play an overwhelming role in the atmospheric emissions of hydrocarbons. Even if we were to control all urban emissions of hydrocarbons, biogenic emissions would still cause some southern cities to exceed the national ambient air quality standards for ozone.

Chemical Processes - Land

Glaze prefaced his remarks by noting that the principal problem we face as environmental scientists and engineers is not what approach we need to take to solve these important problems, but that we simply do not have enough money to address these issues. It is incumbent upon us to convince the policy-makers of this over-riding limitation.

He noted that many of the processes used for the treatment of soil are often based on very little data. From a national perspective, soil treatment is a multimillion dollar business based on very little science. It is very empirical, with little chemistry known about these processes. For example, we know very little about what happens when hydrogen peroxide is injected into the subsurface to stimulate biological activity. We don't know the by-products of this combined chemical and biological activity because of limitations in our analytical chemistry capabilities. Hence we are unable to perform meaningful risk assessments.

Such analytical limitations also prevent us from fully being able to characterize groundwater contamination at hazardous waste sites. Many chemicals can go undetected and unidentified. It is frightening to think that many hazardous materials are being overlooked because of our limited analytical capabilities. Sooner or later, we will see the significance of these unidentified contaminants when we do risk assessments and biological scientists make use of tools that don't discriminate via a list of individual compounds prepared by a regulatory agency.

Schwarzenbach, in his discussion, noted that in the United States, most of the research in this area is geared to assessment and control of contaminants based on their impact on human beings. In Europe, a higher priority is placed on the protection of ecosystems than is in the US.

He also pointed out, with regard to the oxidative treatment processes discussed by Glaze, that we don't know what kinds of changes might take place as a result of using advanced oxidation processes. Will things get better or worse? This same point was echoed in the floor discussion which followed, supporting Glaze's earlier contention that too little is known about the science underlying many of the proposed soil treatment schemes. It was noted that the by-product issue will be with us for as long as we employ chemical and biological oxidation processes.

Paul Roberts (Stanford) added a significant point, i.e., that the time scale in groundwater transport is important with regard to chemical processes. Because of the slow nature of transport processes characteristic of groundwater systems, chemical processes may be very important even though some of them may be very slow.

Chemical Processes - Water

Rather than discussing the full range of chemical research needs in aquatic environments, O'Melia focused his presentation on his own interests in interfacial chemistry and the role played by organic macromolecules in controlling particle behavior in aquatic systems. His comments included deposition and aggregation kinetics, and colloidal transport in aquifers. He noted that, in his opinion, despite many years of research by many scientists and engineers on the nature of particle surfaces, the electrical double layer, and particle-particle interactions, the kinetics of unfavorable particle deposition and aggregation reactions have not been modeled with any confidence by any person at any place or time. There is a definite need to model particle-particle interactions and the behavior of particle-associated contaminants, but this effort is confounded by macromolecules and their configuration at particle surfaces.

Eisenreich, in his discussion, catalogued several important research needs associated with particles and organic-solute interactions in natural aquatic systems. He pointed to the importance of particle dynamics in understanding chemical transfer in natural waters, and to the significant role played by sediments in being the repository of contaminants previously introduced into water and their role as a source and sink of such contaminants.

In view of the focused nature of the formal presentations, the discussion from the floor was also focused on interfacial phenomena. It was noted that ionic strength and the nature of functional groups associated with organic molecules play a central role in the degree to which various anionic and cationic contaminants associate with particles and with sorbed organic macromolecules. O'Melia indicated that the interaction of these macromolecules with contaminants is influenced by the presence of solid phases. Macromolecules do not occupy a very large portion of the available surface area, i.e. there are still plenty of surface sites available even in the presence of natural organic material. It was pointed out by another discussant that bacterial adhesion to surfaces usually occurs on less than 0.2% of the available surface area, via colonization in the form of micro-colonies.

Biological Processes - Introduction

C.P. Leslie Grady, Jr.
Department of Environmental Systems Engineering
Clemson University
Clemson, SC

A major change has occurred in environmental engineering since the last workshop on research needs. It is the realization of the interrelatedness of all of the processes occurring in the environment and in our treatment systems. Whereas we previously tended to focus on biological processes as if they were unaffected by physical and chemical events, that is no longer the case. Our increased interest in hazardous and toxic materials has made it very clear that factors such as solubility, volatilization, susceptibility to hydrolysis or photoylsis, and adsorption onto solids all have major impacts on the biodegradability of organic compounds in the environment. As a result, we have gained a much more integrated approach to the solution of environmental problems, and that approach has been apparent in the presentations preceding this session.

The presentations in this session also emphasize the interrelatedness of environmental processes. In particular, Alexander Zehnder will address biological processes in the soil, where interactions with solid surfaces are extremely important. For most of us, working in the soil matrix is a new experience and adds a level of complexity to which we are unaccustomed, in spite of our recognition of the importance of physical/chemical interactions. Even when we return to our traditional water matrix, however, as Sandra Woods will point out, we can no longer treat biological events as if they were isolated.

Although the other sessions all address events occurring in the air, it is difficult to envision biological processes impacting on it directly (although they certainly have indirect impacts). Consequently, we have not considered it here, but rather, have used the time to address an important discipline that is having an increasing impact on environmental decision-- risk assessment. It is an area with which we should all become more familiar, and to introduce it to us we have asked Michael Gough to address its use with respect to toxic materials.

Biological Processes - Risk/Toxicology

Michael Gough
Center for Risk Management
Resources for the Future
1616 P Street, NW
Washington, DC 20036

Les Grady called me in April and invited me to come here to speak about what research is needed in environmental toxicology during the next ten years. He also asked me to discuss how that research might impact on environmental policy and how engineers and researchers might interact to increase the probability of progress. Well, that was April, and November seemed a long way off, and I agreed. As November came closer, Les called to remind me that I owed him a paper, and I wondered what I could say in 15 minutes to cover the three topics he'd mentioned. That problem became somewhat simpler when I remembered that policy and research in risk assessment are often so intertwined as to make their separation almost impossible.

I will begin my discussion about research and policy by talking about risk assessment for carcinogens. Almost all signs indicate that we are in a transition period. Three years ago, the Office of Science and Technology Policy in the White House published a long paper in the Federal Register that reviewed what was known about chemical carcinogens and described how Federal agencies evaluated those substances (OSTP, 1985). A year later, the Environmental Protection Agency (EPA) published a Federal Register notice titled "Guidelines for Carcinogenic Risk Assessment" (EPA, 1985).

Both documents state that Federal agencies will routinely assume that carcinogens present a risk of cancer at any exposure level and that extrapolation models can be used to estimate how risk varies with dose. I think it worthwhile to emphasize the word "assume" in that sentence.

We, of course, do not know whether or not risk exists at very low doses. Since we don't know, there are good policy reasons for behaving as if it does. One upshot of that policy decision is a standard, I can even say, a cookbook, approach to risk assessments for carcinogens. All suspect chemicals are tested under a standard protocol that requires exposure of groups of rats and mice to two doses of a suspect chemical. The results of that test are then fed into a standard linearized multistage model that predicts the frequency of cancer in humans exposed to 1 milligram of the chemical per kilogram of body weight per day for their lifetimes. From that number it is a simple exercise to calculate the daily dose that is associated with a 10^{-6} lifetime risk of cancer.

Those steps and calculations are made regardless of whether or not the carcinogen interacts with DNA and regardless of what is known about the biological activity of the chemical. Furthermore, whether the data are weak or strong, or whether they make or don't make sense from a biological standpoint, the risk numbers are published in the same list, suggesting that all are equally valid.

To their credit, both the OSTP and EPA documents acknowledge that great uncertainties accompany assessing risks for carcinogens, and they say that other methods might be appropriate under some circumstances. On the face of it, mentioning other methods suggests that the agencies are flexible about which method might be used for a particular chemical. That, however, is not the case. The guidelines are rigid because they give no guidance about when the use of other methods might be appropriate. Without that guidance, in my opinion, risk assessments will almost always follow the standard procedures. Certainly, any deviation from the standard procedures requires a great deal of justification and the hurdles are so high that few will be attempted.

Despite that rigidity, a lot has changed. Within the last year, EPA has lowered its estimates for the cancer risks associated with dioxin, arsenic, methylene chloride, and hormones and hormone-like substances that cause thyroid cancers. In all those cases, the agency deviated from its own guidelines. (Subsequently, the EPA's Science Advisory Board decided that the dioxin revision was not justified, and the old estimate has been enshrined.)

The document that describes EPA's 17-fold reduction in its estimate of the carcinogenicity of dioxin contains a figure that displays estimates of the carcinogenic potency of dioxin as determined by regulatory agencies in different countries (EPA, 1988). Several countries use a threshold model to estimate dioxin's potency, and those models predict no human risk at exposures up to more than 1000-times higher than the exposure that EPA associates with a 10^{-6} lifetime risk of cancer. EPA did not embrace the use of a threshold model, but it did consider results from it alongside results from the linearized multistage model. In my opinion, that consideration accords threshold models a degree of regulatory respectability that was formerly lacking.

More directly to the question of thresholds, EPA has stated flat out that there are safe exposure levels--thresholds--for hormones that cause thyroid tumors (EPA, 1988a). None of the information that EPA relied upon to conclude that the hormones have carcinogenic thresholds was obtained or is obtainable from standard tests for carcinogenicity. Instead those data come from experiments in research areas such as biochemistry or molecular biology.

I think the reevaluated carcinogenic potencies are harbingers of the reintegration of toxicology into the experimental biological sciences. Although some toxicologists have always done research that you and I would call biochemistry, immunology, molecular biology, or some other basic biology discipline, Congressional and public emphasis on testing has largely pushed the non-routine, investigative aspects of toxicology into the background. Despite relative inattention to basic research because of the focus on testing, insights and conclusions from such research are so persuasive that they have forced modification of potencies estimated from standard carcinogenic risk assessments.

In turn, the reevaluations of carcinogenic potency, which depend on basic biology, are affecting policy. EPA (1988b) announced in August that it is reopening discussion of its guidelines for carcinogenic risk assessment. That reconsideration will provide an opportunity to incorporate provisions for the use of new information in risk assessments.

My conclusion from all this is that the next few years will see more importance being given to basic research findings in the evaluation of carcinogens. The standard approaches will still be with us, and for some substances they may suffice. But when a chemical represents a class of compounds for which better understanding of biological impacts is important or when a chemical is economically important, I expect to see much greater consideration given to facts and inferences from basic science.

I also expect many objections to consideration of information that is not obtained by the standard methods. The objections will probably center on contentions that the standard ways are "good science," and that the new information is obtained from "unproven techniques." Those objections will have great currency because 10 or 15 years ago we knew so little that we had to depend on assumptions. In the intervening years, those standard techniques, because of repeated use and regulatory dependence on them, have become accepted as the way to do things. Nevertheless, they were not firmly based on science. And even had they been, it is a hallmark of science that opinions and conclusions change as methods of investigation and the resulting data change. It is neither scientific nor good policy to reject insights from science that couldn't be done years ago and to depend on assumptions that were necessary years ago because the science wasn't mature enough.

One problem that was with us a long time ago remains with us today. How do we, or how should we, extrapolate from results of animal studies to make predictions of human risks? EPA has, for almost a decade, relied upon the linearized multistage model, and its main competitors have been models that appealed to the minds and hearts of statisticians rather than being based on biology. During that same period of time, Moolgavkar and Knudson and their colleagues have championed a different model that is based on one of the best understood human cancers.

About half of the 1,000 cases of retinoblastoma, a cancer of the retina, develops in children under 3 years of age. Most babies are born with two functional copies of the RB gene, but those who are to develop retinoblastoma during infancy inherit one damaged and one normal gene. Some event subsequent to birth inactivates the normal gene and when both are inactive, cells in the retina grow out of control and become cancerous. The active RB gene, then, can be considered to be an antioncogene.

Moolgavkar bases his extrapolation model on these findings and argues that there are two critical mutation events in carcinogenesis (Moolgavkar, 1986; Thorslund et al. 1987). Although the retinoblastoma story has been important for Moolgavkar's model for extrapolation, it seemed that the role of the RB gene itself was limited to a rare cancer. That is no longer the case.

Lee et al. (1988) and Harbour et al. (1988) reported this summer that some breast and lung cancer cell lines fail to make RB protein. Those findings, by themselves, do not say anything about causality. It could be that deranged growth of tumor cell lines leads to the disappearance of the RB proteins, but the frequency of RB^- cells among primary breast cancers, small cell lung cancers, and pulmonary carcinoid is about the same as found in retinoblastomas (Marx, 1988). Their presence in primary tumors supports the idea that there is a causative role for the RB^- genotype (or phenotype). Furthermore, two unrelated transforming viruses, adenovirus (Whyte et al. 1988; Weinberg, 1988) and SV40, produce proteins that interact with and inactivate the RB protein. This finding also supports the conclusion that the RB protein is involved in carcinogenesis. It is very attractive to think that the RB protein normally restrains cell growth, but when the RB gene ceases to make the protein or when the protein itself is inactivated by cancer virus activities, the restraint on cell growth is lost. In steps that are not yet clear, the loss of that restraint eventually progresses to a tumor.

The RB gene and protein are not involved in all cancers. For instance, there is no evidence for inactivated RB gene in types of lung cancer cells other than small cell and pulmonary carcinoid tumors. Of course, it is immediately apparent that some other gene may play the antioncogene role in other cell types.

Laboratory biology is not the only likely source of new information for use in regulatory decisionmaking. Epidemiology, especially around waste disposal sites, may become a major contributor of information. Many academic epidemiologists have shied away from such studies because of the difficulties of estimating, much less measuring exposures, and because of what appear to be low exposures. Only very rarely does the prospect of doing a study that is likely to turn out negatively excite anyone as much as doing one that is likely to be positive. In addition, it is more difficult to obtain funding for likely-to-be negative studies. To some extent, inattention to those studies is ending. Public concern about exposures from waste sites has prompted Congress to provide money for them.

I share the biases of academic epidemiologists. I think that very few health effects will be demonstrated around waste sites. At the same time, I think those studies can provide information that is unavailable from other sources. In particular, negative studies will provide information about what exposure levels are not associated with health effects.

The usefulness of those studies will very much depend on the accuracy of estimation or measurement of exposures. I am not familiar enough with exposure measurement techniques to have specific suggestions for research, but I am convinced that the value of the government-supported epidemiology will be directly related to how well exposures can be estimated. One subset of that problem especially intrigues me.

What sorts of conversions do chemicals undergo in the environment over time? In turn that leads to another question. Do we estimate or measure exposures to the parent chemical or to conversion and degradation products? Those questions and all the related problems of fate and transport could usefully involve collaboration between engineers and biologists.

That's my first mention of collaboration, and I will close my talk with a little discussion of that subject. I think of engineers as practical, pragmatic people. Paul Deisler, a chemical engineer and former vice president of Shell, has talked for years about the impossibility of extrapolating over three or four or five or six orders of magnitude. He's almost certainly right. I think that that pragmatic position, which is certainly shared by many others, has kept the problem of selecting a model or models for extrapolation from being shoved into a neat cubby labeled "solved." Only by keeping a problem as a problem rather than declaring it to be solved can we expect any progress.

Engineers are also going to be involved in solving or moving to solution of the exposure estimation problems. Not only because of their interest in hardware, but also, I think, because those problems either have solutions or they don't. We look to systematic, pragmatic people to assess problems like that.

Risk assessment is, finally, breaking out of rigid assumptions that have constrained it. Once the assumptions are left behind, some practical questions become interesting from a regulatory as well as the scientific viewpoint. What cellular genes are involved in cancer? How are they affected by chemicals? By viruses? What do the answers to those questions tell us about extrapolation from animal results to estimates of human risk? What are background exposures? What are exposures near waste sites and other risky areas? How do we find out? Which chemicals do we assess? Which do we worry about?

There's plenty of room for collaboration. And plenty for questioning what our colleagues in other disciplines are doing.

References.

Environmental Protection Agency (EPA). 1986. Guidelines for carcinogenic risk assessment. *Fed. Reg.* 51:33992-34003.

Environmental Protection Agency (EPA). 1988. A Cancer Risk-Specific Dose Estimate for 2,3,7,8-TCDD. USEPA: Washington EPA/600/6-88/007Aa.

Environmental Protection Agency (EPA). 1988a. Thyroid Follicular Cell Carcinogenesis: Mechanistic and Science Policy Considerations. SAB Review Draft. USEPA: Washington. EPA/625/3-88/014A.

Environmental Protection Agency (EPA). 1988b. Intent to review guidelines for carcinogen risk assessment. *Fed. Reg.* 53:32656-32658.

Harbour, J.W. et al. 1988. *Science* 241:353-356.

Lee, E. et al. 1988. *Science* 241:218.

Marx, J.L. 1988. *Science* 241:293-294.

Moolgavkar, S.H. 1986. *Ann. Rev. Pub. Health* 7:151-169.

Office of Science and Technology Policy (OSTP). 1985. Chemical carcinogens; a review of the science and its associated principles, February 1985. *Fed. Reg.* 50:10372-10442.

Thorslund, T.W. et al. 1987. *Risk Analysis* 7:109-119.

Weinberg, R.A. 1988. *Scientific American.* Sept. 1988, pp. 44-51.

Whyte, P. et al. 1988. *Nature* 334:124-129.

Discussion: Biological Processes - Risk/Toxicology

Joseph V. Rodericks
ENVIRON Corporation
Washington, D.C. 20007

Michael Gough has captured the central problem in risk assessment and, in calling for an increasingly prominent role for basic biology in identifying and measuring risks, he has picked the right solution to it. There is surely no likelihood of progress in either toxicology or risk assessment as long as we continue to rely solely upon standardized (typically whole animal) test systems for the collection of the information that is used to infer human risks. Elucidation of underlying biological processes appears to be essential if we are truly to understand how animal data are to be extrapolated to humans, across exposure routes, and from high-to-low dose exposures (i.e., to those that typically are encountered in the environment). Until these processes are understood, we shall probably continue to treat these forms of extrapolation generically--i.e., the same extrapolation models will continue to be applied to all substances in a relatively rote manner, in an attempt to achieve apparent consistency. I suggest, however, that we shall see only very slow movement away from standardized procedures in toxicology and risk assessment. My pessimism is based on prior experience in and with regulatory agencies. These agencies are reluctant to rely upon non-standard methodologies that need to be tailored to individual substances. From the point of view of the regulatory agencies, the only practical means to manage the hundreds, if not thousands, of individual agents subject to regulation is to standardize testing and assessment methods. It is unlikely that we shall move away from "black box" approaches until these agencies are convinced of the generic applicability of new methods that can be relatively well standardized. On the other hand, the research community can do much to push regulatory agencies in the right directions, and the types of developments in basic biology Dr. Gough has so well summarized are beginning to be felt.

Biological uncertainties are important, but equally important are the uncertainties regarding the nature and magnitude of human exposure to environmental agents. It is in the latter area that the opportunities for engineers to contribute to needed improvements in risk assessment are most apparent. The risk assessor cannot travel far without understanding the relationship between releases of chemicals to the environment and the amount, frequency and duration of human intake of them and their degradation products. Reliable data and models for exposure assessment are as important to risk assessment as are data and models for hazard and dose-response assessment. Issues of particular concern in exposure assessment are: representativeness of analytical measurements of environmental samples; reliability of transport and fate models; nature and quantities of degradation products; pattern and distribution of exposures in affected populations; frequency and magnitude of human exposure to contaminated media; and rates of contaminant uptake and absorption by humans.

The quantitative effect of various remedial or exposure reduction measures is another critical piece of information for the risk assessor and decision-maker and my experience suggests that this is another area of much-needed research.

Biological Processes - Land

Alexander J.B. Zehnder
Department of Microbiology
Agricultural University
6703 CT Wageningen
The Netherlands

Introduction

Soils and sediments have been and still are the ultimate dumping place of all wastes from our society. Air pollutants, which do not escape to the stratosphere or are not eliminated in the atmosphere by chemical or photochemical reactions "disappear" in the soil. Polluted river water which infiltrates into the groundwater, leaves behind parts of the pollutants adsorbed onto soil particles. Pollutants in lakes, estuaries and oceans are eventually buried in the sediments. In addition, soil is the only place to dispose solid wastes. Unlike in the atmosphere and in aquatic systems, the dispersal of pollutants in soil is very slow and the mean residence time is extremely long. This slow dispersal has, for a long time, restricted the pollution problems to a local level, and since the negative effects of pollutants were not evident at the soil surface, the soil was believed to possess a high "buffer capacity". The slow dispersal and the restriction to a local level were the main reasons for the almost entire absence of a public concern about soil pollution until very recently.

The increasing negative impact of polluted soils on the groundwater quality and incidences like Love Canal have made soil protection a political issue. As a result, engineers and scientists began to investigate the possibilities for the clean-up of polluted soils and groundwater. Among others, question was raised about the potential of microorganisms to remove pollutants. It was and still is surprising how little is known about microbial processes in soil and in a complex soil matrix. In contrast to aquatic systems, the soil is highly heterogenic with respect to the spatial distribution of substrates, nutrients and microorganisms (1) but also with respect to various phases and interfaces. Therefore I would like to investigate in the next five years as a first topic:

The influence of solid surfaces and interfaces on microbial activities in soil.

The final fate of a pollutant depends on whether it is degraded or not. Consequently, it is important to know if microorganisms present in the soil are able to degrade a given compound or have the capacity to eventually "learn" to degrade such a chemical. To obtain a satisfactory answer to these questions, information is needed about the influence of environmental conditions (pH, redox, surfaces, presence of other organisms, etc.) on specific microbially mediated reactions. Hence, the second research topic I would like to deal with is:

The potential of soil microorganisms to adapt to new conditions which are the result of changes in physical, chemical and/or biological parameters of the environment.

For quantitative predictions of the fate of pollutants it is necessary to possess kinetic data on the breakdown of a given compound or class of compounds obtained under different conditions (temperature, pH, redox, presence of other substrates and organisms, etc.). A kinetic parameter that has both environmental and toxicological importance is the threshold. The threshold of a chemical is the concentration below which it is not degraded anymore. Thus, the third topic which I feel should be investigated in more detail in the coming years is:

Degradation kinetics in multi-organism and multi-substrate systems, in particular factors influencing the extent of the thresholds.

In the following these three topics will be discussed in the light of (i) their importance to obtain basic information on the biological, in particular microbial, processes in soils, (ii) what specific questions should be asked and investigated, (iii) the spin-offs that might be expected for other research areas and disciplines, and where applicable, (iv) the manner in which results from this research may be used to help formulate rational environmental policies and/or more effective control strategies.

Microbial activities at interfaces and solid surfaces

Soils and sediments consist largely of particles of variable sizes. These particles are responsible for the presence of large areas of interfaces, in particular solid/water and in the case of terrestrial soils also solid/air and water/air. It has been shown that over 99% of the microbial activity in soil was found in connection with solid surfaces (2). It is therefore not exaggerated to state that microbial processes in soil take place almost exclusively on the surface of soil particles. In microbiology it is common practice to study microbial processes in homogeneous, aqueous systems. Solid surfaces are excluded whenever possible. During quantitative investigations, e.g. in a chemostat, all precautions are taken to prevent surface growth. As a consequence most mathematical models in microbiology can only be applied to homogeneously dispersed systems. Only very recently models for non-homogeneous and non-dispersed systems have been developed (3, 4).

For a thorough understanding of soil microbiology, the effect of the presence of a solid surface on the behaviour and metabolism of microbes must be systematically elucidated. The most basic questions which have first to be answered are: How do bacteria adhere to surfaces? How do bacteria attach to surfaces? Once these questions have been answered satisfactorily, the main topic can be tackled, which is the physiological, biochemical and genetic mechanisms triggering adhesion and attachment. With the results from this research it should be possible to answer the questions about the manner in which interfaces and solid surfaces influence microbial activities.

Much research has been done on microbial adhesion. A clearcut unifying theory is lacking yet but it becomes increasingly evident that the DLVO-theory can adequately describe the physical-chemical process of microbial adhesion to soil particles (5). Once microorganisms adhere, they may actively anchor to the surface using various sorts of polymeric extrusions (e.g. polysaccharides) or appendages (e.g. pili and fibrils). The medical literature contains a considerable amount of information about the mechanism of attachment of pathogenic and non-pathogenic microorganisms to tissues, teeth, implants, etc. (6). Studies on biofilm formation present additional insights into the way bacteria attach to all kind of materials and other bacteria (7). While much is known about how microorganisms attach, our knowledge about the mechanisms triggering adhesion and attachment is almost absent. Data are needed about the effect of environmental parameters on physiological processes in microorganisms and the subsequent expression of specific surface structures such as polysaccharides, etc. These surface structures may also influence the surface properties such as hydrophobicity or electrical charge. Only when adequate information about these regulations are available, can we begin to understand why soil microorganisms, in particular bacteria, adhere and attach to soil particles and what physiological effect (if any) might be induced by the presence of surfaces and interfaces.

Bacterial adhesion and attachment is not only of importance in soil microbiology, but also in (*i*) biotechnology and wastewater treatment where immobilization or coagulation of biomass is wanted, in (*ii*) biofouling, caries formation, and surgery where attachment must be prevented, and in (*iii*) plant-microorganism interactions where, depending on the organism, attachment or detachment is desirable. The complexity of the problems related to microbial activities at interfaces and surfaces is a research area where a close collaboration between basic sciences and engineering disciplines can be extremely profitable.

Microbial adaptation

Soil is an ever changing environment, temperatures can vary from minus 50° to over 50° C, and there is a continuum of water activities and redox conditions. Depending on the state of the environment these conditions can change drastically, e.g. during day-night cycles, rainfalls, droughts, etc. In flooded soils redox conditions may even vary diurnally. All these are typical for surface soils, and continuous changes demand a tremendous adaptive capacity of the microorganism living there. About 50 years ago, man started to vary an additional factor by bringing into the soil alien compounds (mineral oil, xenobiotics, etc.) to which soil microorganisms have never been previously exposed. It became quickly apparent that microorganisms can adapt to a large number of such compounds and are even able to transform or mineralize them. Compounds thought to be recalcitrant some fifteen years ago, suddenly are found to be biodegradable. One might hypothesize that either researchers learned to create the right conditions for the microorganisms, which is probably true for some cases, or some microbes "learned" to degrade specific compounds. Biologists have found some evidence for this "learning" of microbes. Three mechanisms have been described. The first is the activation of genetic information already present in the organism (8). The second involves an alteration in the substrate specificity of an enzyme as a result of a gene mutation induced by mutagenic agents (9). In this case the altered enzyme can now also attack structurally related molecules. The last mechanism consists of a recombination of pieces of pathways from different microorganisms encoded on specific DNA fragments into one microorganism. This recombination allows the final recipient to carry out biochemical reactions which it could absolutely not do before (9). All three mechanisms may occur in nature concomitantly or in any combination.

At the moment we are very far from understanding these processes, especially the natural recombination. A thorough understanding of the adaptation reactions would supply us with information about the ultimate metabolic potential of a given microbial community and would allow us to assess the chance for a soil to undergo self-purification. Based on this knowledge, environmental engineers could decide whether a specific pollution should be treated biologically or not. Therefore I would like to concentrate my future research in this area on the following points: *i* The molecular mechanism of adaptation to new substances, and *ii* The conditions at which this adaptation best takes place.

Results from these investigations are useful for the evaluation of the vulnerability of a given soil to a specific pollutant and its chance to deal with it without help from the outside (self-purification). However, if treatment is necessary the data obtained will indicate the most promising approach. Information from the research done under this topic is also essential for assessing the real risk in cases where laboratory derived, genetically modified microorganisms are to be used in the environment. One of the major concerns in such an application is that genes from the genetically modified microorganisms may find their way into the autochthonous microbial population - just as happens in natural systems without addition of organisms from outside - leading so to undesired effects.

Information from microbial adaptation research is necessary for a realistic formulation of environmental legislation because (*i*) these data offer the fundamental insights not only into the prospects, but also the limits of microorganisms to remove pollutants from the soil and groundwater environment, and (*ii*) as a result of this knowledge, the sensitiveness of a given soil to anthropogenic influence (physical treatment, chemicals, input of alien microorganisms, etc.) and the chances of recovery by adequate treatment or protection measures can be assessed.

The threshold concentration

Once we are aware that a compound is biodegradable it is important for the environmental engineer to know the velocity of this process, and the minimum concentration which can be attained by the action of microorganisms. My research in this field will therefore concentrate on: Quantitative and qualitative effects of environmental parameters (physical, chemical and biological) on the biodegradation kinetics, formation of metabolites, and the threshold concentration.

The most important physical parameters are: temperature, water activity, presence of surfaces and the concentration of compounds at the interfaces (see topic 1), mass transport limitation, degree of inhomogeneity, etc. The chemical environment is composed of other chemicals and their stimulatory or inhibitory (toxic) effects, specific nutrients, pH, availability of certain electron acceptors (redox), etc. Other organisms and their mutualistic, synergistic or antagonistic effects are the biological factors (see topic 2). During the process of biodegradation of organic chemicals, intermediary products may be formed which resist further microbial attack. These metabolites may even be more toxic than the mother compound. In almost all cases, the metabolites are much more soluble and thus also more mobile in soil and aquifers because of their lower hydrophobicity. The change in hydrophobicity is the result of the elimination of non-polar groups or the addition of some polar functions to the molecule. By changing some environmental parameters the release of certain metabolites can be prevented (10).

A solid amount of information is available for a selected amount of compounds with regard to their biodegradation kinetics in the soil environment. We are also learning more and more about the quantitative influence of environmental parameters on these kinetics (11). However, concerning the threshold, our information is quite limited. Selected publications deal with specific aspects of this phenomenon but the biological rational behind the threshold is in most cases not known (12). Therefore, qualitative and quantitative information about the factors affecting it is lacking; e.g. how does the presence of a surface affect the threshold?, what is the influence of a secondary substrate or the adsorption of the substrate itself?, can the presence of certain organisms lower the threshold? etc. It is also important to know whether a threshold for adaptation exists, or in other words, is there a concentration limit below which organisms will no longer adapt to new chemicals? Answers to these kind of questions are essential if polluted soils are to be cleaned-up, or if the harmful effects of contamination must be assessed for soil and groundwater.

Conclusions

In my opinion, future environmental engineering research on biological processes in terrestrial and aquatic soils and in sediments has to be directed to the understanding of some key phenomena on a molecular level. To be successful, the knowledge of the various disciplines concerned should be combined. The integration of the different engineering, scientific, and eventually economic aspects should be done with the appropriate mathematical instruments, viz. modelling. Only with such an approach can the empirical problems of chemical handling and management be overcome and replaced by the rational solution of some of the most urgent problems of the terrestrial environment.

References.

This list is not thought to be complete. These references were selected to provide the interested reader with some more detailed information on certain aspects discussed above.

1. Parkin, T.B., A.J. Sexstone, and J.M. Tiedje. 1985. Comparison of field denitrification rates determined by acetylene-based soil core and N-15 methods. *Soil Sci. Soc. Am. J.* 49:94-99.

2. Stotzky, G. 1985. Mechanism of adhesion to clays, with reference to soil systems. In: Savage, D.C., Fletcher, M. (eds.) *Bacterial Adhesion*, Plenum Press New York, pp. 195-253.

3. Namkung, E. and B.E. Rittmann. 1987. Evaluation of bisubstrate secondary utilization kinetics by biofilms. *Biotechnol. Bioeng.* 29:335-342.

4. Kissel, J.C., P.L. McCarty, and R.L. Street. 1984. Numerical simulation of mixed culture biofilm. *J. Environ. Engr.* 10:393-411.

5. Loosdrecht, M.C.M. van, J. Lyklema, W. Norde, and A.J.B. Zehnder. 1989. Bacterial adhesion: a physicochemical approach. *Microbial Ecol.*, 17:1-15.

6. Mirelman, D. ed. 1986. Microbial Lectins and Agglutins. Wiley Interscience, New York.

7. Costerton, J.W. et al. 1987. Bacterial biofilms in nature and diseases. *Ann. Rev. Microbiol.* 41:435-464.

8. Mortlock, R.P. and W.A. Wood. 1964. Metabolism of pentases and penitols by *Aerobacter aerogenes. J. Bacteriol.* 88:838-844.

9. Ramos, J.L., A. Wasserfallen, K. Rose, and K.N. Timmis. 1987. Redesigning metabolic routes: Manipulation of TOL plasmid pathway for catabolism of alkylbenzoates. *Science.* 235:593-596.

10. Bachmann, A. et al. 1988. Biodegradation of alpha- and beta-hexachlorocyclohexane in soil slurry under different redox conditions. *Appl. Environ. Microbiol.* 54:143-149.

11. Bachmann, A. et al. 1988. Aerobic biomineralization of alpha-hexachlorocyclohexane in contaminated soil. *Appl. Environ. Microbiol.* 54:548-554.

12. Button, D.K. 1985. Kinetics of nutrient-limited transport and microbial growth. *Microbiol. Rev.* 49:270-297.

Discussion: Biological Processes - Land

James M. Tiedje
Department of Crop and Soil Science
Michigan State University, East Lansing, MI

Remediation of soils and sediments contaminated with hazardous chemicals is one of the most challenging problems faced by contemporary society. To be successful will require skills of many scientific and engineering disciplines working in a coordinated manner. One of the least costly remediation mechanisms is biodegradation, if and where it can be made to work. Thus, I believe the major research questions are centered on issues needed to assess the feasibility of bioremediation. Professor Zehnder's three thrust areas address some of these needs, however, I offer a slightly different emphasis.

The key questions that I think need to be addressed are given below in sequential order.

1. Do microorganisms exist with suitable catabolitic potential, and if they exist are they native to the contaminated area? While this is an old topic, what is lacking is new innovation to demonstrate the presence of, or the ability to recover (isolate) useful organisms that may be fastidious, have unusual requirements, or express their activity only at low levels. Considerably more metabolic diversity exists in nature than has so far been isolated. The bloom in reports on new anaerobes is evidence of some of this diversity being uncovered.
2. Will the organism with the desired capacity grow in the contaminated soil or sediment system? Professor Zehnder alludes to a number of physicochemical parameters of the soil environment in his section on adaptation. I think one of the most important areas in which progress is usually possible is to select (or even engineer) biodegrading organisms that are more tolerant to toxic components of the waste mixtures. Resistances to metals are well known and tolerance to solvents and other chemicals are often observed but not well understood. Other biological phenomena important to successful colonization by biological agents are protozoan grazing, phage infection, and the presence of sufficient selective pressure to result in growth. The latter is a particular problem if there is not enough energy released to the organism, such as is often the case for co-metabolism (because the conversions may only be a few steps), and if the substrate yields too little energy, such as is the case for highly chlorinated compounds (e.g. PCP). Research that can lead to better management of these phenomena has been meager.
3. If the organism can live in the contaminated environment, what then becomes the rate limiting

parameter? In a porous matrix the transport that allows the chemical and organism to readily meet is often rate limiting. There are two aspects of this question that are important. One is that our understanding of the rate of release of chemicals that have been aged in the soil matrix is inadequate. For example, a half-equilibration time for EDB in soil was found to be 2 to 3 decades, while freshly added EDB was degraded within one month (1). We have also found that Aroclor 1242 freshly added to sediment is readily dechlorinated while the aged Aroclor in sediment appears to be more slowly degraded (2). Thus the "bioavailability" of the bound materials to the microbial population may be a severe limitation to bioremediation. If so, this requires additional means to solve this limitation. Possibilities are the production of surfactants by the microbial degrader or cost effective physical or chemical schemes to facilitate release. The second aspect is how to foster remediation when the chemical is dispersed over a large area. In this case I believe the focus should be on which is easier to move in the soil matrix: the chemical to be treated, the biodegrading organisms, or perhaps other requirements of the organism such as an electron acceptor. Recent work by Costerton's group (3) has shown that starved microbes can be converted to UMB forms (ultra-micro bacteria), which move much more readily in porous media and provide more hope for improved distribution of bacteria. If it is an electron acceptor that is to be added, then there is more potential for adding nitrate because of its low cost, high solubility and the fact that it is already common in the environment. To do this successfully, however, requires more work on denitrifying bacteria to better identify, understand and improve their biodegradation capacities.

References

1. Steinberg, S.M., J.J. Pignatello and B.L. Sawhey, Persistence of 1,2-Dibromoethane in soils: Entrapment in intra-particle pores. *Environ. Sci. Tech.* 21:1201-1208, 1987.
2. Quensen, J.F., J.M. Tiedje and S.A. Boyd, Reductive dechlorination of polychlorinated biphenyls by anaerobic microorganisms from sediments. *Science* 1988 (In press).
3. MacLeod, F.A., M.M. Lappin-Scott, and J.W. Costerton, Plugging of a model rock system by using starved bacteria. *Appl. Environ. Microbiol.* 54:1365-1372, 1988.

Biochemical Processes - Water

Sandra L. Woods
Department of Civil Engineering
Oregon State University
Corvallis, OR 97331-2302

It is important that environmental engineers develop a fundamental understanding of the biodegradation process to properly select and design water or wastewater treatment facilities and to understand the fate of compounds in aqueous environments. An immense number of compounds are chemically synthesized or unintentionally produced through industrial processes. However, it is impossible to characterize the biodegradation of each of these compounds under every combination of environmental conditions and by every consortia of microorganisms. If we also consider the ability of microorganisms to acquire the competence to biodegrade compounds with acclimation or the loss of competence due to changes in the microbial population or their environment, biodegradation becomes an increasingly difficult process to understand or predict. Therefore, environmental engineers and scientists must develop a sufficient research base to allow us to understand the fate of a compound as a function of its molecular structure and the environmental conditions present. Only by developing generalizations based on fundamental research can we hope to predict the biodegradability of the many new compounds released to the environment each year.

There are two primary components we must systematically study: we must understand (1) how the compound itself and (2) how the environment to which the compound is introduced affect biodegradation. The important variables include but are not limited to:

The Compound

1. The target compound's molecular structure,

2. The target compound's concentration,

The Environment

3. The microorganisms present and their number,

4. Their degree of acclimation and their history,

5. Interactions between microorganisms such as the exchange of metabolic products,

6. The presence of competing electron donors or acceptors and their concentrations,

7. The presence of toxicants, and

8. Other phases which affect the distribution of the target compound, toxicants or other substrates.

Although this list is incomplete, it provides a basis for the factors which need to be understood and provides an indication of the problem's complexity. These factors are important in understanding the biodegradation process not only in aqueous systems, but in all environments.

Environmental pollutants may be degraded as the primary or secondary substrate in a reductive or oxidative process. At a minimum, it is important to understand the manner in which the compound is degraded and how other compounds serve to complete the redox couple. By approaching degradation studies in this manner and by attempting to provide adequate information in research publications to answer these questions, the research base will become much more useful to other researchers as well as consulting engineers or regulatory agency administrators.

The environmental engineering and science community needs information concerning biodegradation pathways and degradation rates to understand the fate of compounds in the environment and to better select processes for the treatment of industrial, municipal or hazardous wastes. Without an adequate understanding of the variables described previously, unit processes may be adequately designed, but they may not be properly selected. Toxic intermediates may accumulate; or biodegradation may not occur at sufficient rates. Although a quantitative description of the degradation process is desirable, unless the factors allowing the achievement of degradation rates in the laboratory are understood, quantitative information is useless and inappropriately applied.

In this paper, three studies are described which attempt to provide some fundamental information concerning biodegradation in aqueous systems. These studies address aspects of variables 1, 6 and 8, above.

Effects of Molecular Structure on the Anaerobic Degradation of Haloaromatic Compounds

Since it is impossible to characterize the biodegradation of every haloaromatic compound and its chemical or biochemical degradation products, environmental engineers and scientists must develop a more basic understanding of the factors affecting biodegradation. The following addresses the effects of the compound's molecular structure, variable 1, on its anaerobic biodegradation.

The anaerobic biodegradation of trace aromatic compounds such as chlorophenols or chlorobenzoates proceeds by reductive dechlorination reactions. The anaerobic biodegradation of chlorophenols occurs by preferential dechlorination of ortho chlorines; and the biodegradation of chlorobenzoates proceeds by preferential dechlorination of meta chlorines. The objective of this activity is to develop a more general understanding of the anaerobic biodegradation of the class of halogenated aromatic compounds by understanding the effects of the position and the degree of halogenation on its degradation pathway and rate.

Hypotheses:

1. The degradation pathway for reductive dehalogenation reactions can be predicted based on the position of the halogen with respect to the other functional groups on the ring. Although the processes of biodegradation and chemical synthesis are fundamentally different, reductive dehalogenation reactions are often observed to occur at the same positions that halogens are

substituted in chemical synthesis reactions. For example, hydroxyl groups are ortho/para directors and chlorophenols are preferentially dechlorinated at the ortho position. Carboxyl groups are meta directors, and chlorobenzoates are preferentially dechlorinated at the meta position.

2. For reductive dehalogenation at a given position (for example, chlorines adjacent to the primary functional group), the rate of the reductive dehalogenation reaction increases with the degree of halogenation.

Benefits: If the order and the relative rate of reductive dehalogenation reactions can be predicted, we may be better able to determine which compounds are most difficult to biodegrade in an anaerobic environment based on the compound's molecular structure. We may be able to predict whether intermediates will accumulate. We may also be better able to design appropriate wastewater treatment processes; and we may provide a basis to better regulate the release of haloaromatic compounds to the aqueous environment by industries or municipalities.

Biodegradation in Multiphase Systems

Unit processes are often designed based upon laboratory research which shows successful, complete biodegradation of a target group of compounds. Yet, complete conversion may not be achieved in the full scale process due to differences in the laboratory environment and in the field. These differences may include the presence of alternate substrates or toxicants. If these compounds are not present, the presence of a nonbiodegradable, nontoxic compound may also affect observed overall degradation rates by creating an additional phase. This additional solid, liquid or gas phase may affect the degradation rate by lowering the effective concentration of the target compound available to the microorganisms in the system. The biodegradation of sorbed trace organic compounds and the kinetics of redistribution of trace toxicants is not well understood and is an important area of study. This activity addresses variable 8, and the objective of this project is to characterize the biodegradation of a trace organic compound in the presence of other phases.

Hypotheses: Biodegradation in a complex system of several phases can be described by creating a mass balance expression and by measuring appropriate constants which describe biodegradation and the kinetics of mass transfer between solid, liquid or gas phases and the aqueous phase.

Benefits: A more thorough understanding of the interactions between mass transfer and biodegradation reactions would improve our ability to predict the fate of organic compounds in the environment and would improve treatment by providing a basis to select and design treatment processes including both physical/chemical operations and biological processes.

Effects of Alternate Electron Acceptors and Donors on Reductive Dechlorination Reactions

Interactions between substrates is one of the most important questions that environmental engineers and scientists must address in developing a fundamental understanding of biodegradation in aqueous systems. This subject addresses variable 6 above. Since compounds released to the environment may be exposed to systems containing several electron donors and acceptors, or may be exposed to these environments sequentially, it is important to develop a research base which will allow us to understand the following:

Case 1. A Simple Case - One Electron Donor, One Electron Acceptor. If an organic compound acts as an electron donor, then we must understand whether it can be degraded in the presence of oxygen, nitrate, or sulfate. Knowledge can be extended to soils, lakes, streams or marine environments. We must develop a general, fundamental understanding of the effects of the concentration of the electron donor and electron acceptor on the degradation rate, toxicity and nutrition. Similarly, if the compound serves as the electron acceptor, we must understand the effect of the structure and concentration of the electron donor on biodegradation.

Case 2. A More Complex Case - One Electron Acceptor, Several Electron Donors. If the target compound serves as an electron donor, we must develop an understanding of the effects of competition by other electron donors on the degradation of the target compound. These effects may simply include inhibition or may change the basic degradation mechanism - allowing the target compound to serve as a secondary substrate.

Case 3. A Realistic Case - Multiple Electron Donors and Electron Acceptors. To understand degradation in aqueous systems, we must understand the complexities of changes in species distribution due to the presence of several substrates, the exchange of substrates between organisms, sequential degradation, toxicity, synergism and many other factors. It is impossible to address this question completely in a single research project or by a single researcher. The complex question presented in Case 3 should be addressed by a group of researchers including environmental engineers, microbiologists and chemists.

Summary

The research "producer" community can assist the research "user" by better defining the important characteristics affecting biodegradation in the laboratory environment. Ideally, the research "producer" should address each of the eight variables described previously. However, this is nearly impossible in many cases. Therefore, the burden of extrapolating laboratory results to the field has often rested on the research "user". The research "producer" community can assist the research "user" through the careful development of research projects on two levels:

1. fundamental studies with simple systems which yield information concerning degradation that can be generalized to other systems (e.g., Case 1), and
2. studies with complex (real) systems which allow the research "producer" and "user" to determine the important environmental factors which affect degradation (e.g., Cases 2 and 3).

Unfortunately, most research projects address Case 1 problems. The research "user" needs the information provided by studies of more complex (real) systems in order to apply research results to environmental systems.

There are many important topics which need to be better understood to facilitate design of treatment processes and to better understand the factors affecting biodegradation in aqueous environments or in soils. Some have been described in this paper. Only through cooperation between environmental engineers, microbiologists, biochemists, and chemists can we hope to understand the processes of acclimation, loss in the ability to biodegrade compounds, inhibition, the survival of genetically engineered organisms, and the very complex problems associated with understanding the differences in field and laboratory studies.

Discussion: Biochemical Processes - Water

Bruce E. Rittmann
Department of Civil Engineering
University of Illinois at Urbana-Champaign
Urbana, Illinois 61801

I begin my discussion by summarizing the four main ideas that I took away from Dr. Woods' presentation. My discussion is contained, in part, in the items that I choose to emphasize as her main ideas. In addition, these four main ideas serve as a springboard for me to add some observations that complement Dr. Woods' presentation.

The first idea is that a fundamental understanding is needed. Hence, research must address mechanisms encompassed by microbiology, ecology, chemistry, and kinetics. Black box approaches no longer suffice.

Second, generalized relationships must be obtained, because there are too many combinations of compounds, concentrations, microorganisms, and environments to study all of them. Research must be directed towards finding the patterns.

Third, the quantitative, mass-balance approach is essential to design and analysis of research, especially when competing reactions, such as phase transfers, are occurring simultaneously with biodegradation.

Fourth, research comprising the first three elements must be multidisciplinary. Various disciplines of engineering and science must be melded together.

My first observation is that biological-process researchers must and will apply the tools of modern molecular biology, chemistry, microbial ecology, and toxicology. We need to be daring enough to explore new techniques (to us) and to forge cross-disciplinary teams. The first key step is that we need to educate ourselves about the tools and how they might be used. Once we know enough to judge a tool's potential value, we can communicate with the experts and work towards a common research approach. This education is hard work and risky; nevertheless, we must devote time and energy to exploring new disciplines.

My second observation is a caution: in our excitement about new research tools from other disciplines, we must not try to become a member of the other discipline. I have noted, especially in younger researchers, a desire to do work that is purely microbiological, chemical, or ecological. Such a temptation, though luring, will not lead to the greatest impact by the environmental researcher. The shortcomings of such an approach are that the environmental researcher: (1) will not be fully accepted by the other discipline, thereby losing scientific impact, funding opportunities, and personal achievement; (2) may sidestep environmental questions, thereby diminishing the practical benefits to our field; and (3) may forego the powerful tools we use, such as mass balances, mathematical modeling, and dimensionless analysis. We must ask how multidisciplinary tools can be brought to bear on our unique issues of environmental biotechnology; becoming something else is not the goal.

My third observation concerns how we reach the "users" of our research: the practicing designers and operators. As our research necessarily becomes more scientific, we run a serious risk of pulling farther away from those who bear the burden of implementing the fruits of our research. In my opinion, we need to devote more time and resources to the translation of research results into practice-oriented information. Researchers and research funders must allot time and money for the task of research translation to practice. Communications to practitioners must take its position alongside of communications to research peers.

Finally, researchers and research funders must continue to investigate fundamental aspects of biological treatment when the treatment is not oriented towards hazardous materials. Dr. Woods' presentation gave three examples, all of which concerned chlorinated organic pollutants. However, there are numerous real problems and scientific questions that involve more conventional pollutants. Some key examples include:

- reliable operation of activated sludge processes, especially concerning suspended-solids separation and bulking control.
- stability and reliability of biofilm processes, especially those used to obtain very high volumetric loadings.
- capture and biodegradation of colloidal organic matter, which usually comprises the majority of wastewater BOD.
- kinetics of the biodegradation of low concentrations of natural organic polymers, which constitute most of the organic fraction of biological-process effluents, natural waters, and drinking water supplies.

In conclusion, biological-process researchers and their funders need to be open to apply new tools for fundamental research about environmental biotechnology, need to make research translation a goal, and need to work on conventional issues, as well as the new issues of hazardous pollutants.

Summary Discussion - Biological Processes

C.P. Leslie Grady, Jr.
Department of Environmental Systems Engineering
Clemson University
Clemson, South Carolina

Risk Assessment

The floor discussion following Michael Gough's paper was both spirited and broad ranging, indicating that environmental engineers are very concerned about how to make assessments about the effects of pollutants on both man and other species in the environment. The discussion made it clear that this concern stems from a desire to make rational and balanced decisions about the level of chemicals that can be released to the environment without adverse effects.

Among the interesting points to arise from the discussion were the following. Society does not have a balanced approach to accepting risk. Although familiar risks (e.g., the automobile) are readily accepted, others, such as potential carcinogens, are less readily accepted. Nevertheless, there is evidence that regulators recognize the impossibility of achieving zero risk for environmental contaminants and are moving toward rational ways for accepting small finite risks. One possible cause for the dichotomy in the public acceptance of risk is failure on the part of the scientific community to effectively communicate with the public concerning risk. In order to reverse that trend, there is currently a large interest on the part of NSF and EPA on the subject of risk communication. A shortcoming of current risk assessment thinking is its anthropocentricity, but there is also evidence that this is changing and that a greater concern is being expressed about life forms other than humans. In spite of that anthropocentricity, however, much of the data that has been collected about the mechanisms of human cancer, etc. is now being applied to understand tumors in other species, such as fish. One approach that was once thought to hold great hope for assessing the risk associated with chemicals was to deduce their carcinogenicity from mutagenicity data. As more data have been collected, however, that correlation has turned out to be weak and thus of limited usefulness. A problem associated with most toxicity and carcinogenicity data is that they are for single compounds. Unfortunately, at this time we have very little information about the impacts of mixtures of chemicals. This is a major factor limiting the development of risk assessment for environmental contaminants, which almost never exist as single compounds. An alternative approach to the study of environmental exposure is to use epidemiological studies, but epidemiology can't evaluate risk at the level that regulators would like to limit exposure. In spite of all of these limits and problems, however, it is clear that risk assessment is becoming a more and more important tool in environmental science and engineering, and one that the members of AEEP should become more expert in.

Land

One of the fundamental changes that has occurred in environmental engineering practice and research in the past few years is the focus on contaminated soils and aquifers. Unfortunately, the microbiological exposure of most environmental engineers has been limited to aquatic microbiology and thus they are not fully aware of the subtle, but important differences associated with the soil environment. In order to accelerate understanding of soil microbiology and the important questions associated with biodegradation in soil systems, soil microbiologists working in the area of biodegradation were invited as both speaker and discussant.

As one might expect, the majority of the discussion focused on surfaces and their impact upon biodegradation, particularly of compounds of low solubility which would tend to adsorb to those surfaces. For example, it is not uncommon for biodegradation rates in soils and aquifers to be limited by rates of desorption. Consequently, the need was recognized for greater interchange of information between those who traditionally work in the areas of sorption and surface chemistry and those who focus on biodegradation. Surfaces probably also play an important role in the interchange of genetic information, and therefore in the development of degradative capability, by providing a stable platform on which plasmid exchange can occur. It was noted, however, that attachment of organisms onto surfaces may also hinder such exchange when population densities are low. Attachment of organisms onto surfaces also has a large effect on the spread of degradative capability in an aquifer or contaminated soil site. For example, if organisms are strongly attached, how can they be mobilized to move within the zone of contamination? There are many unanswered questions about this topic and thus we are not yet in a position to devise effective strategies to facilitate the spread of degradative capability. Consequently, current ideas have focused on ways to deliver capable organisms to multiple sites. Finally, we need to incorporate the patchiness of metabolic capability into our models of contaminant fate if we want to accurately predict the outcome of various remediation strategies.

Water

The discussion following the presentations on biological processes in water reflected well the current state of research activities - torn between traditional problems and approaches and the new opportunities offered by recent advances in microbiology and molecular biology. Although techniques such as gene probes offer great promise for better understanding of biological processes, the danger exists that our research will become so esoteric that no one other than researchers will be able to understand it. At that point we could be accused of ceasing to be engineers with a primary focus on problem solving. Consequently, there was considerable discussion about the need for collaboration between microbiologists and engineers so that the engineers can benefit from the new techniques while retaining their problem-oriented focus. The point was also raised that we still have many interesting traditional problems to solve and that those problems can also benefit from application of new biological techniques. Just because there is currently a large focus on biodegradation of toxic/hazardous xenobiotic compounds, there should not be a cessation of effort on problems like liquid:solid separation or colloidal substrate biodegradation. Rather, environmental engineers should continue to attack the broad range of environmental problems to which biological processes can be applied while working more closely with those who can make our research more effective by applying new tools.

Multiphase Systems - Introduction

Perry L. McCarty
Department of Civil Engineering
Stanford University
Stanford, California 94305

The Earth is a multiphased system. This is true whether we consider the Earth as a whole or view it at a microscopic level. Even the smallest living systems, represented by bacteria, exist in a multiphased world. Microorganisms in the natural environment are often attached to another solid phase and surrounded by a liquid. Indeed, if they are not also in contact with a gaseous phase, they may create one of their own. Methanogenic bacteria when working at their most rapid rates can produce a volume of methane gas equal to their own volume every minute. The phase transfer and transformations of contaminants that occur at this level are important when evaluating their overall movement, transformations, and effects in the environment. Also significant in the fate of contaminants is the role played by solids, liquids, and gases in groundwaters, the soils above, and the vadose zone between. Surface waters also cannot be characterized as single phase systems as they are bounded by solid and gaseous phases, and contain particulate solids and gases within them. The same is obviously true with the air.

On the largest scale of oceans, continents, and atmosphere, contaminant movement, formation, transformations, and effects are obviously of major concern, and may have the most profound effects on the fate of the Earth itself and the ecosystems it supports. This is evident in the growing concern over stratospheric ozone depletion and the greenhouse effect. Thus, knowledge of multiphased systems and the major role they play in the fate and effects of environmental contaminants is of major importance to environmental engineers and scientists no matter what particular phase of the environment they may be concerned with at any given moment, nor what may be the scale of that concern.

Not only must multiple phases be considered in determining the movement and fate of contaminants, but also the range of physical, chemical, and biological processes that occur within or at the boundaries between the phases. It became obvious through the presentations and discussions during the first three sessions of this conference that it is difficult to adequately discuss individual processes occurring within single phases without consideration of the important interactions that occur between other phases and with other processes. Thus, the importance of the more general topics addressed in this last session has already been recognized. Even within this last session, an attempt has been made to compartmentalize the three major phases with individual presentations on air, land, and water. Finally, a presentation and formal discussion on systems as a whole is presented. A lesson to be gained from this session, if it is not already obvious, is the great need for both multidisciplinary and interdisciplinary efforts between engineers and scientists in order to address the greatly complex and yet highly significant environmental problems before us.

Atmospheric Intermedia Transport Processes

Yoram Cohen
Department of Chemical Engineering, and
National Center for Intermedia Transport Research
University of California, Los Angeles
Los Angeles, California 90024

Introduction

Pollutants released to the environment are distributed among the many environmental media such as air, water, soil, and vegetation, as the result of complex physical, chemical, and biological processes. The possible environmental impact associated with chemical pollutants is related to their concentration levels and persistence in the various environmental compartments. Therefore, information regarding the migration of pollutants across environmental phase boundaries (e.g., air-water, soil-water) and their accumulation in the environment is essential if we are to assess the potential environmental impact and the associated risks.

It is clear however, that the large number of current and future pollutants precludes detailed experimental multimedia evaluation of the potential impact of each chemical on the environment. Therefore, mathematical models of pollutant fate and transport have become increasingly attractive, because they offer a relatively rapid and inexpensive assessment of potential hazards. Furthermore, such theoretical models are often the only source of guidance for predicting complex environmental events. Although the multimedia approach to analyzing environmental risk and pollution control strategies is attractive (Chem.Eng.Progress, June 4, 1984), its implementation is hampered by major obstacles. First, the lack of specific multimedia data bases of pollutant concentrations prevents a clear demonstration of the multimedia approach and the validation of transport and exposure models used in multimedia analyses. Second, there is still a serious deficiency in our understanding of various intermedia transport processes (chemical and biological). Consequently, many of the existing multimedia approaches employ highly approximate treatment of intermedia transport processes. Therefore, there are uncertainties in the predictions of pollutant fate and transport models associated with the various intermedia transport processes.

Despite the above difficulties, the multimedia approach is the logical approach for a comprehensive and integrated environmental management (Cohen, 1986a, 1987; Draggan et al., 1987). At the research level the multimedia approach is an important tool in guiding research efforts on intermedia transport. For example, multimedia analysis can be used to determine pollutant transport pathways that are least significant based on mass balance, exposure and risk assessment considerations. Also, multimedia analysis may establish which intermedia transport parameters are known to a sufficient accuracy for environmental applications and which parameters require further refinement.

In this paper we focus only on the major intermedia transport processes that are associated with the atmospheric compartment of the environment. A brief overview of these interactions is provided and the research needs in the various areas are highlighted. Furthermore, the research needs discussed in this review pertain primarily to organic pollutants which comprise the majority of known man-made pollutants. The conclusions drawn here and the suggestions for future research are drawn from the author's research experience on the multimedia and intermedia transport of pollutants.

The Atmospheric Environment: General Description and Intermedia Interactions

Many chemicals are introduced to the atmospheric environment by direct release (Table 1), by evaporation from aquatic or terrestrial environments, from resuspension of dust and soil particles or through aerosol formation from aquatic bodies. After entering the atmosphere a pollutant is affected by various meteorological phenomena such as wind and precipitation that transport it to various regions of the atmosphere and in some instances back to the aquatic and terrestrial environments (see Table 2 and Figure 1).

The atmosphere is a complex dynamic region of the environment. Air circulation, humidity, and temperature vary constantly throughout the various regions of the atmosphere. There are numerous atmospheric flow models that can be used to treat convection and dispersion processes throughout the atmospheric region (Turner, 1970; Hanna, 1973; Stuart and Wendell, 1974; Culkowski and Patterson, 1976; Niuwstadt and Van Dop, 1982; Seinfeld, 1986; Bonzaountas and Fiksel, 1982; Pasquill and Smith, 1983). The subject of the dynamics of the atmosphere and atmospheric dispersion is beyond the scope of this paper. Nonetheless, it is worth noting that the knowledge base in this area probably exceeds or meets the requirement of intermedia and multimedia modeling efforts at least for the next decade. In contrast, information on intermedia transport processes, such as dry-deposition and precipitation scavenging are still in the development stage (Pruppacher et al., 1983a, 1983b; Cohen, 1986a; Cohen and Ryan, 1986c).

TABLE 1
Release of Chemicals to the Atmosphere

i. Stack emissions during manufacturing processes
ii. Fugitive volatilization from various sources including leaks, storage tanks vents, waste disposal and treatment sites.
iii. Losses during use and disposal operations.

The atmosphere may be divided into several regions based on temperature (Heicklen, 1976). The lower region, called the troposphere, is of primary interest in multimedia transport modeling, since most compounds enter the troposphere and are either degraded or transformed in that region. Few organics are likely to persist in the higher stratosphere because of the high energy ultraviolet radiation present there (McEwan and Phillips, 1975).

TABLE 2
Interaction of the Atmosphere with the Aqueous and Terrestrial Environments via Intermedia Transport

Transport from the atmosphere to land and water:

- Dry deposition of particulates and gaseous pollutants
- Precipitation scavenging of gases and aerosols
- Adsorption onto particulate matter and subsequent wet and dry deposition

Transport from water to atmosphere:

- Volatilization
- Aerosol formation at the air-water interface

Transport from soil to the atmosphere:

- Adsorption onto soil particles and transport by wind erosion
- Volatilization from soil and vegetation
- Resuspension of contaminated soil particles by wind

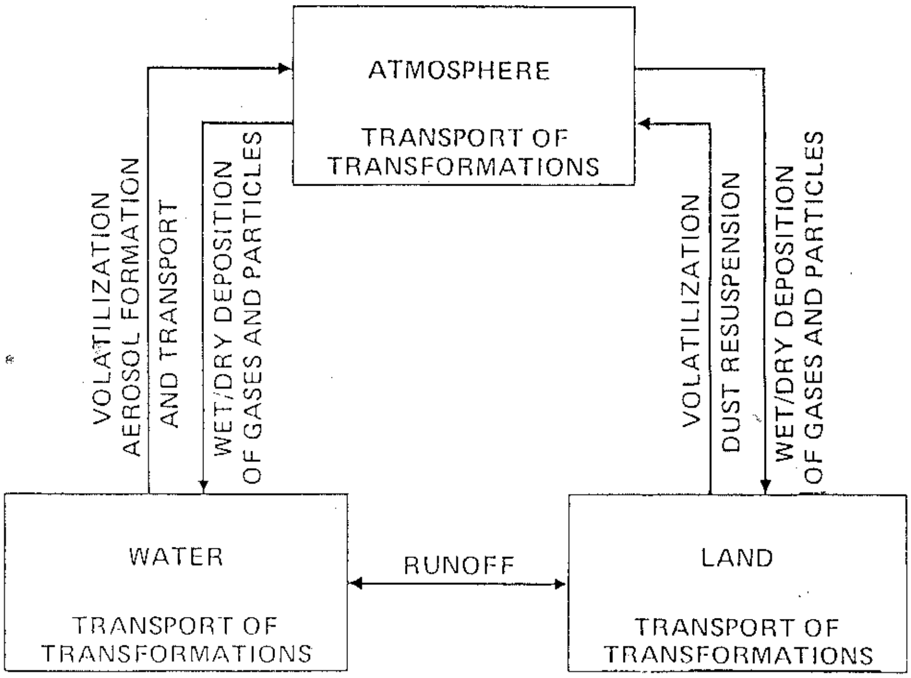

Figure 1: Pollutant Transport from the Atmosphere to Land and Water Compartments

The movement of chemical pollutants into different regions of the atmosphere occurs at different rates (Singh, 1979; Derwent, 1982). The convective half-life associated with movement from the troposphere to the stratosphere is of the order of several decades (about 10-30 years). The convective half-life for transport between the northern and southern troposphere is of the order of one year. The half-life associated with mixing within the troposphere is about one month. Mixing time scales on a smaller geographical scale are much shorter, of the order of a few hours to several days.

The lifetime of pollutants in the atmosphere is strongly affected by their chemical reactivity in both the gas and aerosol phases. Compounds in the atmosphere may react by at least three types of processes (McEwan and Phillips, 1975; Lymann et al., 1982; Darnall et al., 1978; Finalyson and Pitts, 1976; Hampson and Garvin, 1977): 1) direct photolysis by sunlight, 2) electronic energy transfer, and 3) reaction with various species normally present in the atmosphere. Very long reaction times will lead to stratospheric sinks with dry deposition and wet deposition becoming important (Bjorseth and Lunde, 1979). At short residence times, the nature of any resulting reaction products may become important in determining the resulting concentrations in urban and industrial areas.

The fate of organic chemicals in the atmosphere is particularly complex, since many organics are present in both the gaseous and particulate forms (Cantreels and Canwenberghe, 1978). Furthermore, under some conditions, photochemical and thermal reaction can transform the parent compound into more or less toxic daughter compounds (Pitts, 1978). Additionally, significant reintroduction of organics from soil and water bodies into the atmosphere, by volatilization of even low vapor pressure compounds, may occur (Glotfelty and Caro, 1975; Cohen et al., 1978; Cohen, 1983; Cohen et al., 1988).

Due to the complexity of atmospheric interactions with the aquatic and terrestrial media, and the lack of physicochemical information and a source data base for many organic contaminants of interest, atmospheric mass balances are available for a limited number of organic compounds such as DDT (Woodwell et al., 1971; Cramer, 1973; Harrison et al., 1970), PCP (McClure, 1976), B(a)P (Abrott et al., 1978; Cohen and Ryan, 1986), trichloroethylene (Cohen and Ryan, 1985), chloroform (Khalil et al., 1983; Abrott et al, 1978), and formaldehyde (Thompson, 1980).

Dry Deposition

The study of the transport of particles and gases from the atmosphere to solid or water surfaces via dry deposition is fundamental to our ability to describe the dynamic partitioning of pollutants in the environment. If the aerosol deposition velocity is known as a function of particle size, and the chemical composition of the aerosol as a function of size is also known, the rate of chemical deposition can be calculated. Although the subject of dry deposition of ambient aerosols has received much attention in the literature, there are still severe uncertainties in the prediction of deposition velocities as a function of particle size and surface characteristics (Pruppacher et al., 1983a; Slin, 1983a; Sehmel, 1983a; Friedlander, 1987).

Our present knowledge of the mechanisms controlling dry deposition is derived largely from careful studies conducted in wind tunnels. Disagreements between this knowledge base and field experience suggests that different mechanisms may operate in the field and in the laboratory. It is conceivable that closer attention should be paid to the characterization of the turbulent field and its relation to the mechanisms controlling dry deposition.

Adequate predictions of chemical fluxes via dry deposition will require the development of accurate methods of integrating the dry deposition behavior over individual surfaces present in a given terrain. Although there are numerous studies in the above area, uncertainties in both theoretical predictions and experimental measurements are often significant. There is a need to improve our understanding of the relation between the dry deposition velocity and surface properties, while minimizing the need for empirical factors. In this regard, experimental studies with well defined surface elements under controlled conditions may help to elucidate the role of various surface structural properties.

There is also a need for accurate methods of determining the deposition velocity of different organics in the field. The dual tracer technique developed at the NCITR (Friedlander, 1987) may be a particularly useful method for predicting the deposition velocity using source/receptor data.

Finally, there is a need to improve current understanding of the physics of resuspension so that airborne concentrations at respiration heights can be predicted adequately. Current multimedia models rarely include resuspension in the model formulation, primarily due to the large uncertainties associated with current prediction methods.

Wet Scavenging

The scavenging of gaseous pollutants by rain has been extensively studied. There are numerous models that are capable of accounting for effects arising from altitudinal variations in pressure, the mixing ratio of the scavenged species, relative humidity, and temperature (Pruppacher et al., 1983b; Walcek and Pruppacher, 1984a, 1984b; Topalian et al., 1984; Walcek, 1982). Theoretically, given the reaction kinetics in the aerosol and gaseous phases, and the air/water partition coefficient for a given pollutant, one can then predict the rate of rain scavenging. The problem in predicting the rain scavenging rates of organics however, is that the above information is often lacking for many of the organics that have been identified in rain water (Kawamura and Kaplan, 1983, 1984; Steinberg et al., 1984). Moreover, the aqueous phase chemistry of the multicomponent organic mixtures that develop in rainwater is poorly understood (Kaplan, 1987). For example, recent studies have shown that hydrogen peroxide plays an important role in the oxidation of organic substances, NO_x and O_2 (Kaplan, 1987).

Precipitation scavenging of particles is an important process for the removal of particles from the atmosphere (Engelmann et al., 1966). Unfortunately, existing theoretical models for the collection efficiency underpredict the collection efficiency of submicron particles by one to two orders of magnitude (Ryan and Cohen, 1986; Radke et al., 1977, 1980). For example, recent theories have shown that the electrostatic charge associated with the falling rain drops can significantly affect the value of the collection efficiency (Graedel et al., 1983; Barlow and Latham, 1983; Pruppacher et al., 1983a, 1983b). To date, field studies have not succeeded in correlating precipitation scavenging data with accessible and measurable field parameters that account for the effect of electrostatic charge on the particle collection efficiency. Furthermore, in order for rain scavenging field studies to be useful they should report the simultaneous concentrations of the pollutants being tracked in the rain and air phases, as well as the evolving particle size distribution and the chemical mass distribution in the air phase. Such experiments are not trivial and will require much effort to implement.

Finally, tracking organics compounds in rain water can be an important and useful way to trace the sources of atmospheric pollutants. For example, studies in the Los Angeles area (Kaplan, 1987) have revealed that during periods of heavy release, the rain contains benzoic acids, phenols, short chained carboxylic acids and complex mixtures of uncombusted, but thermally altered, hydrocarbons. When the pollutant contribution to the atmosphere is low, the main constituents in the rain are long chain fatty acids and long chain simple paraffinic hydrocarbons, which are derived from plant debris.

Another major roadblock to determining rates of wet and dry deposition of organics is the general absence of accurate quantitative analytical methods for organics in the aerosol phase. The problem of aerosol analysis is particularly difficult since composition must be determined as a function of particle size. Although the analysis for organics in aerosol has been reported in the literature (Lamb, 1980; Simoneit, 1986) none of the analytical methods provide enough information to identify and determine the concentration of each species in the aerosol mixture. Past experience has shown that detailed speciation can account for only about 5% of the organic component of aerosols. For structural characterization to be useful in organic deposition studies, it is essential that the characterization represent a larger fraction of the material. There is room and a need to develop the appropriate analytical tools for determining the chemical composition of organic aerosols and the chemical mass distribution in the particulate phase. For example, recent analytical methods which are based on FTIR analysis appear to be promising, but further refinement of such methods will be needed (Dangler et al., 1987).

The Soil-Atmosphere Interface

Volatilization from soils is the predominant loss mechanism for many low solubility organic contaminants (Hamaker, 1972; Jury et al., 1984a, 1984b, 1984c; Cliath and Spencer, 1972). Volatilization processes are governed by diffusive transport in the soil and by aerodynamic factors operating at the soil/air interface (Farmer et al., 1972; Cohen et al., 1988). The transport of pollutants to the atmosphere may also occur by the resuspension of particulate matter (Pruppacher et al., 1983a, 1983b; Travis, 1975). Pollutants may also be transported to water bodies through runoff and subsequently back to the atmosphere via volatilization.

The rate at which pollutants volatilize from the soil is determined by a number of factors which include the retardation of the chemicals via adsorption and chemical transformations. While various correlations exist to estimate contaminant adsorption onto the soil solids (Karickhoff, 1981), the dependence of the adsorption isotherms on temperature is known only but for a very limited number of pollutants (Cohen et al., 1988). Additionally, information on the chemical and biotransformations of organic chemicals in the soil environment is often lacking. Thus, it is difficult to accurately predict the migration of most contaminants across the soil/atmosphere interface.

Theoretical soil transport models generally assume uniform temperature and moisture profiles in the soil matrix. In addition (Bonazountas, 1983), most experimental studies have been confined to isothermal conditions and at uniform moisture distribution throughout the soil columns that were employed. In the environment however, significant temperature and moisture gradients exist in the top soil (about the first top centimeters). Thus, significant effects of temperature and moisture variations on contaminant diffusion can be expected. For example, recent studies have shown that the volatilization flux varies diurnally (Cohen et al., 1988). Thus, calculations of exposure associated with contaminated soils (i.e., hazardous waste sites) should incorporate the above transport behavior.

In order to employ transport models which properly account for moisture and temperature variations, there is a need to develop an appropriate theoretical framework that will allow the prediction of the dynamic temperature and moisture profiles in the soil environment (in the upper unsaturated soil zone). Current theories are incapable of providing quantitative predictions of the diurnal variations of temperature and moisture in the top soil zone.

The Air/Water Interface

Pollutants may enter the aqueous phase from the atmosphere via precipitation scavenging, dry deposition of aerosols, and gas absorption as described in the previous sections (Slinn et al., 1978; Pruppacher et al., 1983a, 1983b; Cohen et al., 1986b). Chemicals may leave the water phase to the atmosphere by volatilization and by aerosol formation (Blanchard, 1982).

A variety of methods to predict the air/water mass transfer coefficient in natural water bodies are now available (Cohen, 1983; Mackay and Yeun, 1983, Brutsaert and Jirka, 1984; Cohen and Ryan, 1985). The calculations of volatilization/absorption fluxes require data on the air/water partition coefficients in natural waters. Such data are often lacking although the experimental methodology for determining these data are available (Mackay et al., 1979). Also, the application of current methods such as UNIFAC to the prediction of air/water partition equilibrium has received some attention and should be further pursued.

The available prediction methods, however, do not consider the effect of naturally occurring soluble surface active chemicals (Parker and Barsom, 1970). Also lacking is information on the effect of microbial and chemical activity, in the sea surface layer, on the transport of pollutants, gaseous exchange and photolysis. Additionally, the transport of pollutants from aquatic bodies to the atmosphere through the formation of aerosols and via spray transfer (MacIntyre, 1974; Blanchard, 1982; Broecker and Siem, 1984; Newery and Merlivat, 1984) is inadequately documented at this time.

The Plant/Atmosphere Interface

Plants are the basic food components in the food chain to humans, hence their role as mobilizers and sinks of pollutants is particularly important. Plants may absorb and transport pollutants from the soil to the atmosphere or absorb pollutants from the atmosphere (Nash, 1974; Wallace and Berry, 1981; Rundel, 1987, 1988; Hosker and Lindberg, 1982). Pollutants may also deposit on shoots of plants, and they may be taken up through plant leaves. A schematic diagram of the interactions of the plant compartment with the atmosphere and the soil environment is shown in Figure 2.

The zone beginning at the root surface and extending far into the bulk of raw soil, with its biota (i.e., rhizosphere) is very active microbially. In this zone, transformations and mobilization of mineral nutrients and pollutants occur. Thus, pollutants may be chemically or biologically transformed before becoming available to plants.

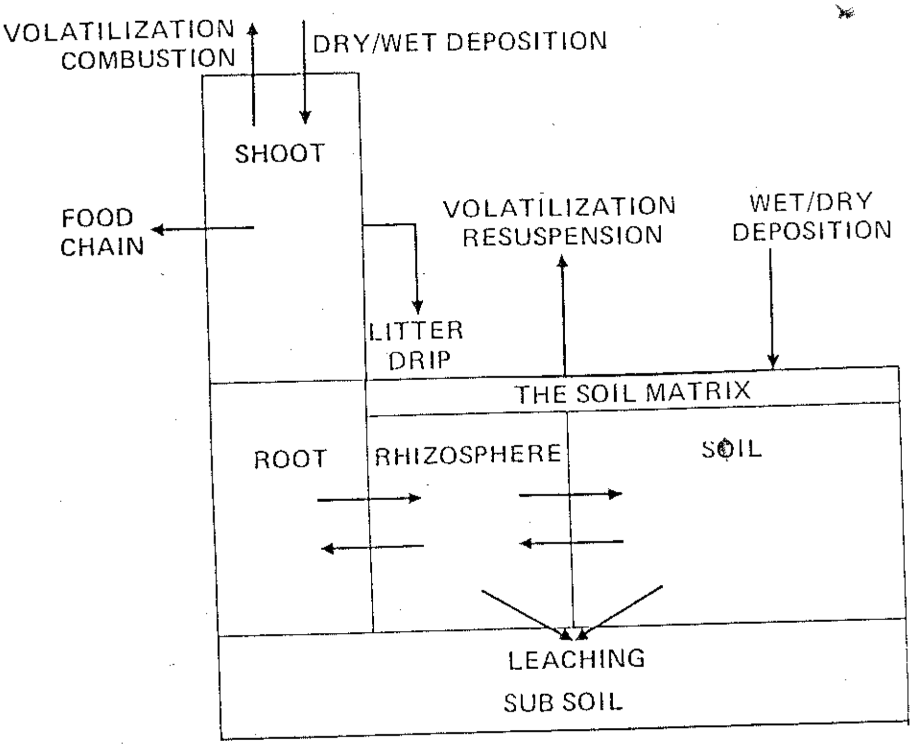

Figure 2: Exchange Processes at the Plant/Atmosphere and Plant/Soil Interfaces

A variety of studies have demonstrated that different plants are sensitive to gaseous and particulate pollutants (Rundel, 1987, 1988; Bounpragob, 1987). For example, one of the ongoing studies at UCLA (Rundel, 1987) is designed to investigate leaf chemical characteristics that regulate foliar exchange and sorption of gases and particles. This particular study focuses on developing an understanding of the fluxes of atmospheric inputs of selected pollutants into the natural desert ecosystem along the eastern margin of the main pollutant plume from the Los Angeles basin. There is a large number of studies that have shown that dry deposition onto leaf surfaces is a strong function of the surface microstructure of the leaf. The above studies, and other recent studies on the fundamentals of dry deposition onto rough surfaces suggest that there is also a need to develop a fundamental understanding on the microsurface characteristics that affect dry deposition onto leaf surfaces. Furthermore, since vegetation surface is often heterogeneous there is a need to understand how to describe dry deposition onto rough but spatially heterogeneous surfaces.

Summary of Research Needs

Although there are numerous unanswered questions regarding pollutant transport associated with the atmospheric environment, the following summary of research needs addresses only those key issues which affect the inclusion of the atmospheric compartment in an integrated multimedia scheme of describing pollutant transport in the environment.

1. The role of wet and dry deposition in the transport of organic pollutants is still subject to many uncertainties and it warrants further research.
    a. Experimental work on measuring and correlating the chemical composition distribution for various organic chemicals in the aerosol phase is needed. Such information is required in order to develop a capability for predicting the rates of wet and dry deposition of organic pollutants.
    b. Fundamental work is needed on dry deposition of submicron particles onto rough surfaces. What is needed are fundamental studies that are focused on relating the deposition process to measurable microscopic surface properties.
    c. There is a need to develop and validate methods to integrate deposition velocities across spatial inhomogeneities in rough terrains, and in vegetative covers.
    d. The area of particle resuspension should receive more attention especially in view of the importance of resuspension in affecting particle concentrations in the respiration height.
2. Basic work is needed in order to assess the role of the water surface microlayer in intermedia transport and the multimedia cycle of various chemicals in the environment.
3. Aerosol formation at the air/sea interface has to be carefully examined in order to quantify the effect of this mode of transport on the overall multimedia partitioning of pollutants.
4. Research effort should be devoted to revealing the mechanism controlling mass transfer at the leaf/atmosphere interface. While there have been numerous experimental studies on the subject and various empirical correlations have been proposed, there is still room for basic research aimed at providing a sound theoretical framework.
5. Further research is needed in order to build the knowledge base on the multiphase transport of chemicals in the unsaturated soil zone under the effect of diurnal moisture and temperature variations. At the same time improved theories of non-isothermal energy and moisture transport in porous media are needed in order to allow accurate predictions (or simulations) of diurnal temperature and moisture variations in the soil matrix.
6. The evaluation of health risks, based on multimedia exposure, is subject to numerous uncertainties involving the possibility of multiple exposure pathways, multiple pollutants, and the associated toxicological response. Scientific uncertainties often plague many of the assumptions of quantitative risk assessment (QRA). Often, it is unclear how these uncertainties propagate through the analysis of QRA. Thus, there is a need to develop acceptable methodologies of quantifying and incorporating modeling, parametric, and data uncertainties into the process of intermedia and multimedia risk assessment. Sound scientific methodologies will have to be developed to track the propagation of uncertainties and to develop uncertainty measures that could be used in risk management.

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References.

Abbrott, T.J., M.J. Barcelona, W.H. White, S.K. Friedlander, and J.J. Morgan, "Human Dosage/Emission Source Relationships for Benzo(a)pyrene and Chloroform in the Los Angeles Basin", Special Report to US/EPA, Keck Laboratories, Caltech (1978).

Barlow, A.K. and J. Latham, "A Laboratory Study of the Scavenging of Sub-Micron Aerosol by Charged Raindrops", Pruppacher, H.R., R.G. Semonim and W.G.N. Slinn, "Precipitation Scavenging, Dry Deposition, and Resuspension", Vol. 1 - Precipitation Scavenging Proceedings of the Fourth International Conference, Santa Monica, California, 29 November-3 December, 1982. Elsevier, New York (1983).

Bjorseth, A., and G. Lunde, "Long-range Transport of Polycyclic Aromatic Hydrocarbons," *Atmos. Environ.* 13:45 (1979).

Blanchard, D.C., "Aerobiology and Water-Air Exchange," ASRC Report, 1979-81, Atmospheric Sciences Research Center, State University of New York at Albany (1982).

Bonazountas, M., "Soil and Groundwater Fate Modeling," in "Fate of Chemicals in the Environment," Swann, R.L. and A. Eschenroeder (Eds), ACS Symposium Series No. 225, American Chemical Society (1983).

Bonazountas, M. and J. Fiksel, "ENVIRO: Environmental Mathematical Pollutant Fate Modeling Handbook/Catalogue," EPA No. 68-01-5146, Arthur D. Little, Cambridge, MA (1982).

Bounpragob, K., "Seasonal Effects of Air Pollution on the Physiology of the Lichen *Ranalina menzieseii*, Ph.D. Thesis, University of California, Los Angeles (1987).

Broecker, H.C. and W. Siem, "The Role of Bubbles for Gas Transfer from Water to Air at Higher Wind Speeds. Experiments in the Wind-Wave Facility in Hamburg," in Brutsaert, W. and G.H. Jirka, "Gas Transfer at Water Surfaces". Reidel Publishing Company, Dordrecht, Holland (1984).

Brutsaert, W. and G.H. Jirka (eds), "Gas Transfer at Water Surfaces". Reidel Publishing Company, Boston (1984).

Cantreels, W. and r. Van Camwenberghe, "Experiments on the Distribution of Organic Pollutants Between Airborne Particulate Matter and the Corresponding Gas Phase," *Atmos. Environ.* 12:1, 133-141 (1978).

Chemical Engineering News, editorial, "Panel Suggests Management Changes at E.P.A.," June 4, 33 (1984).

Cliath, M.M. and M. Spencer, "Dissipation of Pesticides by Volatilization of Degradation Products, I. Lindane and DDT," *Env. Sci. Tech.* 6:910 (1972).

Cohen, Yoram, "Mass Transfer Across a Sheared, Wavy Air-Water Interface," *Int. J. Heat and Mass Transfer* 16:1, 289-297 (1983).

Cohen, Yoram, W. Cocchio, and D. Mackay, "Laboratory Study of Liquid Phase Controlled Volatilization Rates in the Presence of Wind-Waves," *Env. Sci. Tech.* 12:553 (1978).

Cohen, Yoram, "Mass Transfer Across Sheared Wavy Interfaces," *Int. J. Heat and Mass Transfer*, 26, 1289 (1983).

Cohen, Yoram, "Modeling of Pollutant Transport and Accumulation in a Multimedia Environment", in

"Geochemical and Hydrologic Processes and Their Protection", Draggan, S., J.J. Cohrssen, and R. E. Morrison (Eds), Praeger Publishing Company, New York (1987).

Cohen, Yoram, "Organic Pollutant Transport," *Environ. Sci. Technol.*, 20, 538 (1986).

Cohen, Yoram, H. Taghavi, and P.A. Ryan, "Contaminant Diffusion under Non-Isothermal Conditions in Nearly Dry Soils," *J. Environmental Quality*, 17, 198 (1988).

Cohen, Yoram and P.A. Ryan, "Multimedia Modeling of Environmental Transport: Trichloroethylene Test Case", *Environ. Sci. Technol.*, 19, 412 (1985).

Cohen, Yoram and P.A. Ryan, "A Theoretical Analogy of Turbulent Mass Transfer Across Sheared Gas-Liquid Interfaces," *Int. Comm. Heat Mass Transfer*, 12, 139-148 (1985).

Cohen, Yoram (Editor), *Pollutants in a Multimedia Environment*, Plenum Press (1986a).

Cohen, Yoram, "Intermedia Transport Modeling in Multimedia Systems," in *Pollutants in a Multimedia Environment*, Cohen, Y. (Editor), Plenum Press (1986b).

Cohen, Yoram and P.A. Ryan, "Multimedia Transport of Particle Bound Organics: Benzo(a)pyrene Test Case", *Chemosphere*, 15, 21-47 (1986).

Cramer, J., "Model of the Circulation of DDT on Earth," *Atmos. Environ.* 7:(1973).

Culkowski, W.M., and M.R. Patterson, "A Comprehensive Atmospheric Transport and Diffusion Model," ORNL/NSF/EATC-17, Oak Ridge National Labortory, April (1976).

Dangler, M., S. Burke, S.H. Hering and D.T. Allen, "A Direct FTIR Method for Identifying Functional Groups in Size-Segragated Atmospheric Aerosols," *Atmos. Environ.*, 21, 1001-1004 (1987).

Darnall, R.R., A.C. Lloyd, A.C. Winer, and J.N. Pitts, Jr., "Reactivity Scale for Hydrocarbons Based on Reaction with Hydroxyl Radical," *Environ. Sci. Technol.*, 12:317 (1978).

Derwent, R.G., "On the Comparison of Global, Hemispheric, One-Dimensional and Two-Dimensional Model Formulation of Halocarbons Oxidation by OH Radicals in the Troposphere," *Atmos. Environ.*, 16:551-61 (1982).

Draggan, S., J.J. Cohrssen, and R.E. Morrison (Eds), "Geochemical and Hydrologic Processes and Their Protection," Praeger Publishing Company, New York (1987).

Finlayson, B.J., and J.M. Pitts, Jr., "Photochemistry of the Polluted Troposphere," *Science* 192:111 (1976).

Friedlander, S.K., "Dry Deposition," in National Center for Intermedia Transport Progress Report, 1987, University of California, Los Angeles.

Glotfelty, D.E., and J.H. Caro, "Introduction Transport and Fate of Persistent Pesticides in the Atmosphere," in *Removal of Trace Contaminants from the Air*, V.R. Dietz (ed.), American Chemical Symposium Series, ACS, Washington, D.C. (1975).

Graedel, T.E., P.S. Gill, C.J. Weschler, "Effect of Organic Surface Films on the Scavenging of Atmospheric Gases by Raindrops and Aerosols Particles," in Pruppacher, H.R., R.G. Semonim and W.G.N. Slinn, "Precipitation Scavenging, Dry Deposition, and Resuspension," Vol. 1 - Precipitation Scavenging, Proceedings of the Fourth International Conference, Santa Monica, California, 29 November-3 December, 1982. Elsevier, New York (1983).

Hamaker, J.W., "Diffusion and Volatilization," in "Organic Chemicals in the Soil Environment," Gorin, C.A.I. (Ed), Marcel Dekker, New York (1972).

Hampson, R.F. and D. Garvin, "Reaction Rate and Photochemical Data for Atmospheric Chemistry," NBS special publication, 513 (1977).

Hanna, S.R., "A Simple Dispersion Model for the Analysis of Chemically Reactive Pollutants," *Atmos. Environ.*, 7:802 (1973).

Harrison, H.L., O.L. Loucks, J.W. Mitchell, D.F. Parkhurst, C.R. Tracy, D.G. Watts, and Y.L. Yannacone, Jr., "Systems Studies of DDT Transport," *Science*, 170:502 (1970).

Heicklen, J., *Atmospheric Chemistry*, Academic Press, New York (1976).

Hosker, R.P. and S.E. Lindberg, "Preview: Atmospheric Deposition and Plant Assimilation of Gases and Particles," *Atmos. Environ.*, 16, 988-920 (1982).

Jury, W.A., W.F. Spencer and W.J. Farmer, *J. Environ. Qual.*, 13, 573 (1984a).

Jury, W.A., W.J. Farmer and W.F. Spencer, *J. Environ. Qual.*, 13, 567 (1984b).

Jury, W.A., W.F. Spencer and W.J. Farmer, *J. Environ. Qual.*, 13, 580 (1984c).

Kaplan, I.R., "Organic Compounds in Wet Deposition," NCITR Annual Progress Report (1987).

Karickhoff, S.W., "Semi-empirical Estimation of Sorption of Hydrophobic Pollutants on Natural Sediments and Soils," *Chemosphere* 10:833-46 (1981).

Kawamura, K. and I.R. Kaplan, "Organic Compounds in the Rainwater of Los Angeles," *Environ. Sci. Technol.*, 17, 497-501 (1983).

Kawamura, K. and I.R. Kaplan, "Capillary Gas Chromatography Determination of Volatile Organic Acids in Rain and Fog Samples," *Anal. Chem.*, 56, 1616-1620 (1984).

Khalil, M.A.K., R.A. Rasmussen and S.D. Hoyt, "Atmospheric Chloroform ($CHCl_3$): Ocean-air Exchange and Global Mass Balance," *Tellus* 35B:266-74 (1983).

Lamb, S.I., C. Petrowski, I.R. Kaplan and B.R.T. Simoneit, *JAPCA*, 30, 1098 (1980).

Lyman, W.J., W.F. Reehl and D.H. Rosenblatt, "Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds," McGraw-Hill, 1982.

MacIntyre, F., "The Top Millimeter of the Ocean," *Scientific American* 61-77, May (1974).

Mackay, D., S. Paterson and M. Joy, "Applications of Fugacity Models to the Estimation of Chemical Distribution and Persistence in the Environment," in *Fate of Chemicals in the Environment*, R. L. Swann and A. Eshenroeder (eds.), ACS Symposium Series, No. 225, ACS, Washington, D.C. (1982).

Mackay, D., W.Y. Shin and R.P. Sutherland, "Determination of Air-Water Henry's Law Constants for Hydrophobic Pollutants," *Environ. Sci. Technol.*, 13:333 (1979).

Mackay, D., and Y. Cohen, "Comments on the Role of Organic Microlayers in Modifying Gas and Particulate Fluxes at Air-Water Interfaces," *J. Great Lakes Research*, 1, supp. 1, 111-112 (1976).

Mackay, D. and A.T.K. Yeun, "Mass Transfer Coefficient Correlations for Volatilization of Organic Solutes in Water," *Environ. Sci. Technol.*, 17:211-17 (1983).

McClure, V.E., "Transport of Heavy Chlorinated Hydrocarbons in the Atmosphere," *Environ. Sci. Technol.*, 10:1, 223 (1976).

McEwan, M.J. and L.F. Phillips, *Chemistry of the Atmosphere*, John Wiley and Sons, New York (1975).

Memery, L. and L. Merlivat, "Contribution of Bubbles to Gas Transfer Across an Air-Water Interface," in Brutsaert, W. and G.H. Jirka, "Gas Transfer at Water Surfaces". Reidel Publishing Company, Dordrecht, Holland (1984).

Nash, R.G., "Plant Uptake of Insecticides, Fungicides and Fumigants from Soils," in "Pesticides in Soil and Water", W.D. Guenzi (ed.), pp. 257-313, Soil Science Society of America, Ind., Madison, WI (1974).

Nieuwstadt, F.T.M., and H. Van Dop (eds.), *Atmospheric Turbulence and Air Pollution Modeling*, D. Reidel, Boston (1982).

Novotny, V., and G. Chesters, "Handbook of Nonpoint Pollution," Van Nostrand Reinhold, New York (1981).

Pasquill, F. and F.B. Smith, "Atmospheric Diffusion", 3rd ed., Ellis Horwood Ltd., West Sussex, England (1983).

Pitts, J.N., Jr., "Mechanisms, Models and Myths: Fiction and Fact in Tropospheric Chemistry," NASA Reference Publication, 1,022 (1978).

Pruppacher, H.R., R.G. Semonim and W.G.N. Slinn, "Precipitation Scavenging, Dry Deposition, and Resuspension", Vol. 2 - Dry Deposition, Proceedings of the Fourth International Conference, Santa Monica, California, 29 November-3 December, 1982. Elsevier, New York (1983).

Pruppacher, H.R., R.G. Semonim and W.G.N. Slinn, "Precipitation Scavenging, Dry Deposition, and Resuspension", Vol. 1 - Precipitation Scavenging, Proceedings of the Fourth International Conference, Santa Monica, California, 29 November-3 December, 1982. Elsevier, New York (1983).

Radke, L.F., E.E. Hindman and P.V. Hobbs, in "Precipitation Scavenging", Champaign IL, Oct. 14-18, 1974, Semonin, R.G. and R.W. Beadle (eds.), ERDA Symp. Ser., No. 41, (Conf-741002), 425 (1977).

Radke, L.F., P.B. Hobbs and M.W. Eltgrath, *J. Appl. Meter*, 19, 715 (1980).

Rundel, P.W., "Monitoring of Terrestrial Processes in the Long-Term Assessment of Forest Effects: A Mechanistic Approach", in Proceedings of California Forest Response Program Planning Conference", February 22-24 (1987), Pacific Grove, CA, Bicknell, S.H. (Ed).

Rundel, P.W., "Organic Compounds in Wet Deposition", National Center for Intermedia Transport Progress Report, 1987, University of California, Los Angeles.

Rundel, P.W., "Compensatory Responses and Physiological Adjustments to Air Pollution", in W. Winner (ed), EPA Workshop on the Response of Trees to Air Pollution: The Role of Branch Studies (1988).

Seinfeld, J.H., "Atmospheric Chemistry and Physics of Air Pollution", McGraw-Hill, New York (1986).

Seinfeld, J.H., "Air Pollution, Physical and Chemical Fundamentals", McGraw-Hill, New York (1975).

Simoneit, B.R.T., "Characterization of Organic Constituents in Aerosols in Relation to their Origin and Transport: A Review", *Int. J. Environ. Anal. Chem.*, 23-207-237 (1986).

Singh, H.B., L.J. Sala, H. Shigeishi, and E. Scribner, "Atmospheric Hydrocarbons, Hydrocarbons and Sulfur Hexafluoride: Global Distributions, Sources and Sinks", *Science*, 103:899 (1979).

Slinn, W.G.N., L. Hasse, B.B. Hicks, A.W. Hogan, D. Lal, P.S. Liss, K.O. Munnich, G.A. Sehmel and O. Vittori, "Some Aspects of the Transfer of Atmospheric Trace Constituents Past the Air-Sea Interface", *Atmos. Environ.*, 12:2, 55-87 (1978).

Start, G.E., and L.L. Wendell, "Regional Effluent Dispersion Calculations Considering Spatial and Temporal Meteorological Variations", NOAA Technical Memorandum, ERI APRL-44, Air Resources Laboratories (1974).

Steinberg, S., K. Kawamura and I.R. Kaplan, "Determination of Low Molecular Weight Aldehydes in Rain, Fog and Mist by Reverse Phase Chromatography of the 2,4-dinitro-phenyl dihydrozone Derivative," *Int. J. Environ. Anal. Chem.*, 18, 253-266 (1984).

Thompson, A.M., "Wet and Dry Removal of Tropospheric Formaldehyde at Coastal Site", *Tellus*, 31: 376-83 (1980).

Topalian, J.H., S. Mitra, D.C. Montague, A. Quintanar and H.R. Pruppacher, *J. Atm. Sci.*, 1, 325 (1984).

Travis, J.R., "A Model for Predicting the Redistribution of Particulate Contaminants from Soil Surfaces", USERDA LA-6035-MS, Los Alamos Scientific Laboratory (1975).

Turner, D.B., "Workbook of Atmospheric Dispersion Estimates", Protection Agency, Washington, D.C., revised (1970).

Walcek, C., Ph.D. Dissertation, Dept. Atmospheric Sciences, University of California, Los Angeles (1982).

Walcek, C.J. and H.R. Pruppacher, *J. Atm. Chem.*, 1, 269 (1984a).

Walcek, C.J. and H.R. Pruppacher, *J. Atm. Chem.*, 1, 307 (1984b).

Wallace, A. and W.L. Berry, in "Report of the Workshop on Research Needs in Intermedia Transport Processes", S.K. Friedlander and H.R. Pruppacher (eds.), National Center for Intermedia Transport Research, University of California, Los Angeles, April 1-3 (1981).

Woodwell, G., P. Craig and H. Johnson, "DDT in the Biosphere: Where Does it Go?", *Science*, 174:1, 101 (1971).

Discussion: Atmospheric Intermedia Transport Processes

Ronald A. Hites
School of Public and Environmental Affairs
and Department of Chemistry
Indiana University
Bloomington, Indiana 47405

The presence of toxic organic compounds in the atmosphere has recently received considerable public attention. An article in the *Washington Post* (1) uses the term "toxic cloud" to describe the atmospheric movement of organic compounds to the Great Lakes. The Sierra Club has recently issued a report titled "Toxic Air Pollution in the Great Lakes Basin: A Call for Action" (2). The Science Advisory Board of the International Joint Commission (a governmental body of United States and Canadian officials) has addressed this issue as well (3). It seems quite clear that the issue of toxic organic compounds in the atmosphere is and will continue to be of considerable public importance.

There are two aspects to this problem. The first is the simple inhalation of toxic organic compounds by people breathing the air; in general, this is not a major route of exposure. The other aspect is deposition of compounds out of the atmosphere. This can result in high exposures to man. For example, fish in Lake Superior have moderate PCB concentrations as a result of the atmospheric deposition of PCBs to Lake Superior. In fact, 90% of the PCBs to Lake Superior come from atmospheric deposition (2, 3). Thus, it seems quite obvious that a focus on the atmosphere as a media of environmental transport is warranted.

The paper prepared by Professor Cohen is excellent and lays out a research strategy which will move us ahead. The research recommendations are good ones, and I endorse them. I have two specific remarks and one more general comment. The specific remarks first:

It is very important to remember that there are sources of chemicals to the atmosphere other than those listed in Cohen's Table I. Combustion of fossil fuels, for example, releases very large amounts of polycyclic aromatic hydrocarbons, some of which are known to be human carcinogens. Combustion of municipal wastes releases chlorinated dioxins and dibenzofurans into the atmosphere. These compounds are also present in automobile exhaust. We should definitely consider these combustion sources when carrying out mass balances of various materials. In some cases, combustion sources may be the dominant input.

I agree with Dr. Cohen's suggestion that the chemical composition of atmospheric aerosols needs to be studied in detail. There are effective methods for obtaining these data. Liquid chromatographic mass spectrometry is a developing tool which should enable us to gain considerable data on the entire range of chemical species in atmospheric aerosols. The problem here is not the lack of analytical techniques but rather the lack of analytical chemists working in the environmental sciences. Environmental engineers need to reach out to these people and draw them into the solution of important environmental problems. Too often, environmental engineers treat analytical chemists as gatherers of data as opposed to participants in the science.

I now turn to the more general point I wanted to make. The data on which one can base and with which one can validate multimedia models is abysmal. The sophistication of many of these models far exceeds the data with which they can be tested. In some cases, the data that are being used to generate and validate models are incomplete and badly out of date. This problem is frequently exacerbated by the engineering community when they state that it is impossible to measure the necessary data in all of the environmental media for all of the compounds of interest. Therefore, the only solution is to model the various intercompartmental processes. While this statement is quite true, it nevertheless leads to an excessive expenditure of effort on modeling and a deficit of expenditure on data gathering. This view is frequently expressed by proposal reviewers who denigrate proposals on field work with the comment "This is excessive and mindless data gathering." What's needed here is environmental data gathering based on a carefully developed plan. Data gathering is expensive; modeling is cheap. Therefore, there is a tendency to do only the latter. We need to do both.

Let me give one example. The issue of deposition velocity continues to be important. We all now recognize that deposition velocities measured in wind tunnel experiments cannot match the real world. Field data on dry deposition gathered with glycerol coated pans do not accurately simulate the real world either. Thus, more sophisticated field experiments from which one can back calculate the deposition velocities are very important.

I suggest that an important research priority should be the gathering of field data on atmospheric deposition (both wet and dry processes) to medium size lakes (4, 5). The compounds to be studied should be selected carefully based on a variety of sources, perhaps one from a combustion source and one from an industrial source. The field sites should be, perhaps, three in number and selected from representative climatic regions of the United States. Only by carefully gathering data from the real world can we ever hope to improve and judge the validity of the multimedia transport models that are generated.

References.

1. M. Weisskopf, *Washington Post*, March 3, 1988.
2. Sierra Club, 214 N. Henry St. Suite 203, Madison, WI; draft dated March 1, 1988.
3. IJC, Sci. Advisory Bd., "Great Lakes Atmospheric Deposition," Windsor, Ontario, (1987).
4. B.D. McVeety and R.A. Hites, *Atmospheric Environment*, 22, 511-536 (1988).
5. D.L. Swackhamer, B.D. McVeety, and R.A. Hites, *Environmental Science and Technology*, 22, 664-672 (1988).

Environmental Engineering Research on Land Contamination

Donald Mackay
Department of Chemical Engineering and Applied Chemistry
University of Toronto
Toronto, Ontario
M5S 1A4

Introduction

The objective of this paper is to present an account of perceived research needs relating to the environmental contamination of land, while recognizing that land is one important component of the multimedia system of air, water, soil, sediments and biota which comprise our ecosystem. The ideas presented here and the perceived relative importances attached to various projects are entirely the result of personal judgment. Undoubtedly others would assign different priorities. It is hoped that this document will serve at least as a basis for discussion.

The approach taken is to review briefly some of the incentives for understanding how contaminants behave in soil. This is followed by a brief description of the equilibrium, transport phenomena and transformations which contaminants experience when present in soils of various types and under various conditions. I will argue that it is essential that we understand how contaminants behave in soils if we are to implement successful engineering interventions or remedial actions in the hope of modifying behaviour and thus mitigating adverse effects of chemicals. Examples are removing chemicals, hastening their degradation, or rendering them immobile. From this I will draw up a list of research topics which I suggest might be addressed in next five years. Finally are some thoughts on how this research may be used to formulate environmental policies or control strategies and how the research community can assist the user community.

The Incentive

The population density of Canada is about 7 persons/mile^2. In the US it is about 64 persons/mile^2. In the Netherlands it is about 907 persons/mile^2. It is therefore not surprising that those who live at such high densities place much greater value on stewardship of their land resources. I concur with the sentiments of those perceptive people who view us as increasingly moving towards a system of social organization in which we view ourselves as part of the ecosystem, not an exploiter of it. We must place more emphasis on maintaining the viability of the soil environment and protecting it from abuse. As the Dutch ecologist and philosopher Christiaan Huichelaar has said, "Als wij onze lucht vervíulen kmot de wind ons wel te hulp. En vervuilen wij ons water dan wassen de rivieren het weer schoon. Maar vervuilen wij ons erfgoed, onze grond dan helpt niets en niemand ons." This can be translated roughly as: When we foul our air, the wind comes to our help. When we foul our water, the river will wash it clean. But when we foul our ground, our heritage, nothing and nobody will help us.

Soil pollution is thus inherently a very different problem from that of air or water because of soil's inherent immobility. If we irreversibly contaminate large areas or volumes of soil, severe continuing problems will result, incurring enormous inconvenience and cost. Some of the more obvious problems are designing satisfactory stores for hazardous materials in soil, for example, employing landfill systems, and remediating soils which have already been contaminated by organic or metallic substances and thus present a danger to humans or wildlife who live on them. There are legal problems associated with the transfer of ownership of contaminated land from one party to another. The prudent purchaser of industrial land now wishes to be assured that he or she is not adopting a liability for previous contamination. There are many severe groundwater contamination problems which have arisen from inappropriate disposal of materials on land, or in land, from which contaminants flow slowly but steadily across property boundaries contaminating wells, and in some cases causing the threat of explosive conditions.

In summary, there is ample incentive to manage our soils with care and sensitivity and devise engineering procedures for treating contaminated situations.

The Condition of a Contaminant in Soil

Partitioning

When a contaminant is present in the soil it may exist in one of several forms. It may be present as a pure phase, for example, liquid gasoline or a metal oxide. It may be sorbed to mineral or organic matter in the soil. As workers such as Chiou and Karickhoff have shown (2-4), organic matter is particularly important as a sorbent for organic contaminants. The contaminant may also be dissolved in water or "dissolved" in air contained in the interstices of the soil. It is essential to understand this distribution quantitatively. This is essentially a problem in physical chemistry and is usually solved by invoking partition coefficients between water and air, water and mineral surfaces, and water and organic phases. When the contaminant is present in dilute conditions, it is not likely to be present as a pure phase, and is merely in solution in one of these four media. For obvious reasons the agricultural chemical community has undertaken extensive studies of how pesticides and herbicides partition in soil systems. These are reviewed in books such as those edited by Grover (6). This forms an invaluable data base for elucidating the behavior of other contaminants.

Of particular engineering interest and concern are the fractions of the chemical which exist in the mobile air and water phases. It appears if an amount in excess of 0.5% of the chemical is present in either or both of these phases, the chemical may display considerable mobility. It may diffuse through the air space and enter the atmospheric environment by evaporation or it may migrate in solution through the soil vertically or laterally, move to the soil surface or to greater depths and possibly enter groundwater. There has been some success developing mathematical models of this process notably the work by Jury, Spencer and Farmer at the University of California, Riverside (11-14). Simpler, but very useful evaluative models have been produced by McCall of Dow Chemical Company (1). But there remains a need to improve our ability to calculate these partition coefficients especially under conditions in which the soil is fairly dry. It appears that mineral matter has quite different absorptive properties when wet and when dry. The soil is also in a dynamic state of heating and cooling with variable moisture content. Thus, piecing together the picture of the partitioning properties of chemicals in this non-isothermal time and space dependent regime is very challenging. Examples are the studies by Cohen, et al. (15), and Freeman and Schroy (7-9).

Transport

Transport within the soil can be by bulk flow of the liquid substance. Examples are the permeation of gasoline or chlorinated hydrocarbons within the soil and into, onto, or through groundwater. A considerable effort has gone into studying the behaviour of non-aqueous phase liquids in soils, but we are still far from having satisfactory simple models describing these phenomena. The driving forces are not only hydrodynamic, gravitational and momentum, but they are also capillary or interfacial tension in nature. This can give rise to very complicated flow regimes with hysteresis effects. Obviously there are striking differences in behavior if the liquid is denser or less dense than the groundwater.

The chemical can also diffuse through the air spaces of soils being subject to periodic "chromatographic" trapping as it progresses. This process is very important as a determinant of fate of spills of petroleum products, organic solvents and agricultural chemicals in soils. The chemicals may also flow in water, again being subjected to retardation through association with mineral and organic matter in the soil. The rates and velocities of these processes are difficult to measure and predict, especially when the chemical is present as only one component in a complex mixture which affects the partitioning equilibrium. For example, how do the polar substances which are inevitably present in a landfill leachate affect the sorption, partitioning properties and thus the retardation factors which toxic organochlorine chemicals will experience as they migrate through soils? Because of differences in retardation factors these chemicals can migrate at quite different rates, giving an almost chromatographic effect. A good example is the behaviour of soluble methyl-tertiary-butyl-ether, which is used as an octane booster in gasoline and which has the potential to migrate much faster than gasoline in soils.

It is critically important that we measure, review and correlate the physical chemical properties of these chemicals since these properties control partitioning, mobility and fate.

Transformation

Chemicals are also subject to transformation reactions. There may be hydrolysis influenced by pH and catalyzed by metals and organic surfaces. There may be photolytic reactions close to the surface. Most important is biodegradation in which the chemicals are subject to conversion by a complex community of microorganisms that has become established in the soil. Predicting and measuring aerobic and anaerobic biodegradation rates in soils is a formidable task, especially when the chemical is subject to simultaneous evaporation and dissolution.

Terrestrial Biota

It is striking that most environmental models and even assessments of the biogeochemical fate of organic contaminants ignore plants and animals that live on or in soils. This is a serious omission for four reasons.

These biota are critical determinants of the continuing stability of soils. They shape our landscape and strongly influence our climate.

Second, the mass of plant material can be very substantial compared to the accessible mass of soil. The quantity of organic matter with sorbing capacity in a forest in the form of bark and waxy cuticles greatly exceeds that in the surface soil. Further, it is highly accessible to the atmosphere. There is a growing opinion that the prevailing atmospheric concentration of substances such as PCBs is controlled or buffered by soil-plant-air interactions.

Third, vegetation is usually the primary vector for human exposure to toxic chemicals. The route from soil or air to vegetation, to domestic animal, and to meat and dairy product to human is often the dominant route of exposure. This is reflected in risk assessments.

Fourth, there are obvious engineering and economic implications of the growing evidence that atmospheric contaminants contribute to the decline of forests as well as aquatic systems.

In total, the interest in terrestrial biota is increasing and just as a scientific "community" grew of those concerned with water to fish bioconcentration, it appears that a similar "community" is growing in the area of soil-air-vegetation transfer processes. Environmental engineers can contribute to this area, and at the very least must maintain some appreciation of its changing status.

Remediation

If we can understand the fundamental behaviour of the contaminant in the soil, perhaps we can exploit this in subtle ways to encourage the chemical to behave in a less disruptive or damaging manner. Perhaps we can replace the bulldozer with the enzyme. For example, if the chemical is a fairly volatile hydrocarbon subject to evaporation, we can enhance the rate the evaporation and thus protect precious groundwater resources by techniques such as soil venting in which the rate of evaporation is artificially enhanced by drawing air through the soil. It is possible to modify the hydraulic regime in the soil by pumping liquids through the soil and in some cases modify the partition coefficients by the use of solvents or surfactants. For obvious financial reasons the petroleum industry has a very high level of competence in techniques for removing organic materials from soil matrices. If they can recover oil from depths of many thousands of feet surely it should be possible to develop a companion technology which will operate at depths of tens of feet. But, surprisingly little effort has been devoted to such activities. Transformation reactions can also be enhanced by introducing microorganisms which may have specific metabolic capabilities for the chemicals present, or enhancing the growth of these microorganisms by provision of essential nutrients or oxygen.

The treatment of air and water effluent streams has reached a very high level of engineering sophistication. Perhaps, a new and exciting area is *in situ* treatment of soils in which we avoid the expense and inconvenience of brute force excavation techniques but treat soils with subtlety and in place. There are several highly successful and economic soil venting efforts which have removed plumes of gasoline in urban areas, which otherwise would have caused severe disruption. An example is the work of Hoag (5). To successfully implement these engineered remedial interventions it is essential that we understand both the present or natural conditions of the contaminant in the soil, how it will behave if we do not remediate, and the effectiveness of the remediation measures. Perhaps the best approach is to seek out and carefully document case studies of successful soil treatment, just as successful case studies of air and water effluent treatment have been documented over the years. These can then be copied, modified and developed into design procedures by the engineering community.

Some of the research priorities which I perceive as being particularly important in the next five years are listed in Table 1 in no particular order. This list is undoubtedly incomplete.

TABLE 1 Perceived Research Needs

Partitioning:

Reliable physical chemical property data and estimation techniques. Partition coefficient data and correlations for wet and dry soil and mineral surfaces for metals and organics. Kinetics of sorption in soils. Partitioning from complex mixtures, especially the role of polar solutes and electrolytes in modifying partitioning of non-polar organics. Temperature and humidity dependence of these properties.

Transport:

Measurements in laboratory and field of chemical migration in soil, air and water vertically and laterally. Retardation factors in mixtures and as a function of ionic status. Transport phenomena (i.e. phenomena, rates and model equations) of denser and less dense than water non-aqueous phase liquids in partially and fully saturated soils.

Transformations:

Laboratory and field data on chemical transformation rates in soils and correlation with other more readily accessible kinetic data, such as BOD data. Estimation of "half lives". Transformations in groundwater. Measurements of enhancement of biodegradation.

Models:

Development of suites of models describing chemical fate in soils under various conditions. Improvements in the peer review system for models. Transport and partitioning models for air-plant-soil systems. Improved biogeochemical models of atmospheric contaminant interaction with soils and their biota.

Remedial Measures:

Exploration into novel soil remediation/decontamination technologies using air, solvents, biostimulation, immobilization, reaction, etc. Documentation of successful remedial projects. Development of design procedures for implementing remedial measures, e.g. soil venting.

Monitoring:

Improved methods, varying in cost and sophistication, for sampling, analysing and in situ "probing" or "sensing" of soils and groundwater.

Socio-Economic Issues:

Compilation of cost data and estimates for various soil treatment processes. Contributions to the "how clean is clean enough" issue. Development of procedures for auditing the contamination status of land for legal purposes. Risk assessment of human exposure from contaminated soils. Development of educational materials for the public, at the school and college levels.

Promoting and Applying Research

Promoting

Some years ago Dr. DiGiano prepared an excellent document through the AEEP Legislative Analysis Committee titled "Protecting our environment--the need for exploratory research". Organizations such as the AEEP and the NSF have to keep beating the drum that exploratory or fundamental research is critical for providing a basis of knowledge for sound environmental management. It may not appear that measuring partition coefficients between organic carbon and water is going to contribute substantially to better soil management or remediation. But it is from fundamental measurements, interpretation of data and identification of the phenomena that come the design tools for engineering activities. Such research generates the skilled manpower that can attack soil contamination problems, and from whom will come the innovative, exciting, unforseen and thus unplanned-for breakthroughs in science and technology.

It is noteworthy that two recent NAS/NRC reviews emphasized the need for fundamental environmental science. These are "Frontiers in Chemical Engineering: Research needs and Opportunities" edited by N.R. Amundson (1988) and "Opportunities in Chemistry" edited by G.C. Pimetal (1985). If these had been written a decade ago I suspect that they would have contained much less (if any) environmental content. Clearly environmental issues are growing on the scale of social and scientific concerns.

Applying

I believe environmental engineers must go beyond the mere description of soil contamination, and the definition or design of remediation measures but must also address "softer" questions as how clean must a soil be before it can be considered to be decontaminated. The answer to this question is profoundly affected by the mobility or availability and the persistence of the chemical within the soil.

There is an obligation to develop, validate and disseminate a set of mathematical models, design procedures and assessment techniques. These are somewhat analogous to the Gaussian air pollution models which have been so successfully used to control stack emissions to levels which result in acceptable concentrations at points of impingement downwind. Another example is the classical oxygen sag calculations in rivers. We need to develop similar equations, calculation techniques and pictorial representations of the processes applicable to chemical processes in soil. We are fortunate to now live in a world of considerable computer literacy in which many of the difficulties associated with undertaking lengthy and complex calculations have vanished. We can now undertake these calculations rapidly and cheaply and generate data which can be presented to the "customer" in attractive pictorial form. This has to be done with considerable care, responsibility, and subtlety because computers bring the potential to make and hide mistakes. We therefore need new peer review systems for environmental models. I can envisage suites of soil related models which will address issues such as the potential for migration into groundwater, evaporation rates from various soil horizons, and rates of migration in groundwater.

Perhaps most effective as a vehicle for facilitating and improving engineering applications is the documentation of successful case studies in which there is a forthright quantitative description of the nature of the problem, how it was solved, what went right, what went wrong, and how much it cost.

Finally, I hope that the importance of soil processes and soil biota will be reflected in the undergraduate and graduate environmental engineering curriculum. Tomorrow's environmental engineer needs an appreciation of, and a sensitivity for the need for careful stewardship of our soil environment and an appreciation of its key role in our multimedia ecosystem.

References

1. McCall, P.J., Laskowski, D.A., Swann, R.L., and Dishburger, H.J., Estimation of environmental partitioning in model ecosystems, *Residue Rev.*, 85, 231, 1983.

2. Chiou, C.T., Peters, L.J., and Freed, V.H., A physical concept of soil-water equilibrium for nonionic organic compounds, *Science*, 206, 831, 1979.

3. Karickhoff, S.W., Organic pollutant sorption in aquatic systems, *J. Hydraul. Engng.*, 110, 707, 1984.

4. Chiou, C.T., and Shoup, D.T., Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity, *Environ. Sci. Technol.*, 19, 1196, 1985.

5. Hoag, G.E., "The Use of Soil Venting for the Rehabilitation of Petroleum Contaminated Soils", proceedings of the Conference, Environmental and Public Health Effects of Soils Contaminated with Petroleum products, University of Massachusetts, October, 1985, published in "Petroleum in Soil" Colabrese, E. and Kastecki, P. (Eds), Wiley, 1988.

6. Grover, R. (Ed), *Environmental Chemistry of Herbicides*, Vols. I and II, CRC Press Boca Raton, 1987, 1988.

7. Freeman, R.A. and J.M. Schroy. 1984. Environmental mobility of dioxins. Paper presented at the 8th ASTM Aquatic Toxicology Symposium, Fort Mitchell, KY. 15-17 April. ASTM, Philadelphia, PA.

8. Freeman, R.A. and J.M. Schroy. 1985. Environmental mobility of TCDD. *Chemosphere* 14 (6/7):873-876.

9. Freeman, R.A. and J.M. Schroy. 1985. Modeling the transport of 2,3,7,8-TCDD and other low volatility chemicals in soils. *Environ. Prog.* 5(1):28-33.

10. Hamaker, J.W. 1972. Diffusion and volatilization. In C.A.I. Goring and J.W. Hamaker (ed.) *Organic chemicals in the soil environment.* Vol. I. Marcel Dekker, New York.

11. Jury, W.A., W.F. Spencer and W.J. Farmer. 1983. Behavior assessment model for trace organics in soil: I. Model development. *J. Environ. Qual.* 12 (4):558-564.

12. Jury, W.A., W.J. Farmer, and W.F. Spencer. 1984a. Behavior assessment model for trace organics in soil: II. Chemical classification and parameter sensitivity. *J. Environ. Qual.* 13(4):567-572.

13. Jury, W.A., W.F. Spencer, and W.J. Farmer. 1984b. Behavior assessment model for trace organics in soil: III. Application of screening model. *J. Environ. Qual.* 13(4):573-579.

14. Jury, W.A., W.F. Spencer, and W.J. Farmer. 1984c. Behavior assessment model for trace organics in soil: IV. Review of experimental evidence. *J. Environ. Qual.* 13(4):580-586.

15. Cohen, Y., H. Taghavi, and P.A. Ryan. 1988. Chemical volatilization in nearly dry soils under non-isothermal conditions. *J. Environ. Qual.* 17(4).

Discussion: Multiphase Systems - Land Contamination

Philip M. Gschwend
Division of Water Resources and Environmental Engineering
Department of Civil Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

The central goals of our fundamental research in *environmental engineering* should be: (1) to learn how individual environmental processes operate, (2) to compile these process descriptions so that we may consider their simultaneous effects, and (3) to inquire how the environment would respond to various perturbations or engineered alterations. Generally these activities involve development and use of mathematical models, and in the case of land contamination, we must include gaseous, liquid, and solid phases in this modelling effort. Successful assembly of such environmental simulators allows us to recognize which components of our understanding are weakest and to test which factors make the biggest difference to model predictions, hence identifying research needs. These models also enable us to respond to policy makers who are examining questions as to the likely effectiveness of various control strategies in light of the costs of such activities. Finally, multiphase models provide an efficient means to transfer the benefits of our research to the "user" community, consultants and regulators.

When we consider multiphase systems, especially land, we can quickly see several major areas of ignorance which require further research:

(1) First, it is still uncertain what the appropriate physical picture is of the phases moving with respect to one another? For example, are there preferred flow channels through which fluids carry pollutants quickly in the vertical through soil, or do components of the solid phase (e.g., colloids) move within the vertical water flow? Such concerns are highlighted by our inability to explain the appearance of particle-reactive chemicals like pesticides (e.g., Jury et al., 1986) and radionuclides (e.g., Coles and Ramspott, 1982) at depth intervals far in excess of our expectations, based on assumptions of isotropy and two-phase partitioning.

(2) Second, fundamental rate data, appropriate for geochemical conditions, are commonly unavailable. This need for kinetic information is clear because various observations indicate that equilibrium assumptions do not enable multiphase chemical fate models to match observations. For example, Steinberg et al. (1987) recently demonstrated that ethylene dibromide (EDB) exhibits a very slow desorption rate from various soils. Both mass transfer processes and reaction rates remain to be quantified. While some work is still needed to obtain physical chemical properties of chemicals, we have much greater ignorance of fundamental rate data. Further, it is likely that degradation rates are often mass transfer limited (hence the enhanced biodegradability of more soluble, but similarly reactive, hydrocarbons). Thus, research is necessary coupling mass transport of chemicals to agents mediating transformations with rates of actual degradation mechanisms.

(3) Finally, although many multiphase models have been, and will continue to be produced to predict chemical fates in the environment, very little research has been performed in an interactive manner to validate the predictions of these models in the field. Field experimentation is expensive and difficult and even under the best circumstances involves factors which are difficult to control. However, these models are worth little without "real-world" testing of their accuracy and robustness.

References

Steinberg, S.M., J.J. Pignatello, and B.L. Sawhney, 1987. Persistence of 1,2 - Dibromoethane in Soils: Entrapment in Intraparticle Pores, *Environ. Sci. Technol.* 21, 1201-1208.

Jury, W.A., H. Elabd, and R. Reskito, 1986. Field Study of Napropamide Movement through Unsaturated Soil. *Water Resour. Res.* 22, 748-755.

Coles, D.G., and L.D. Ramspott, 1982. Migration of Ruthenium - 106 in a Nevada Test Site Aquifer: Discrepancy between Field and Laboratory Results. *Science* 215, 1235-1237.

Environmental Research Strategies for Multiphase Systems - Water

Jerald L. Schnoor
Department of Civil and Environmental Engineering
The University of Iowa
Iowa City, Iowa 52242

Introduction

The historical emphasis on research in environmental engineering has changed markedly since the turn of the century from sanitation and treatment of conventional pollutants, to man-made toxic chemicals in the global environment. From the early 1900's through the 1960's, we focused on removal of conventional pollutants and preservation of the environment. Landmark legislation was passed around the time of Earth-Day 1970, including the National Environmental Policy Act (1970), the Clean Air Act (1970), and the Federal Water Pollution Control Act (1972). Legislation was the culmination of years of environmental research, technological improvements, and public sentiment congealing at that time.

The 1960's and early 1970's were filled with a major environmental research emphasis on eutrophication. Separate legislation did not result in this case, but some significant changes were affected under the Water Pollution Control Act, including successful international cooperation (the International Joint Commission) and significant point source reductions in nutrient additions to the Great Lakes. After the National Eutrophication Survey was completed by EPA in 1976 and the very successful EPA Lake Restoration Program was implemented, it seemed that eutrophication research became passe in the United States. It was supplanted by toxic chemicals research that continues today.

Often major legislation is passed directly after a research initiative or major crisis. The 1974 Safe Drinking Water Act followed publication of the initial volumes of Drinking Water and Health and the pilot results of the National Drinking Water Survey. The Toxic Substances Control Act of 1976 was precipitated by a kepone spill and contamination of the James River and Estuary. Leachate contamination from notorious dumps and landfills (Love Canal, Valley of the Drums, Rocky Mountain Arsenal, Times Beach, Stringfellow) contributed to the passage of the 1976 Resource Conservation and Recovery Act (RCRA), its 1984 Amendments, the 1980 Comprehensive Environmental Response Compensation and Liability Act (CERCLA) and its 1986 Superfund Amendments and Reauthorization Act (SARA). Due to leachate contamination and increased pesticide usage, a large concern over protection of our groundwater and drinking water has arisen.

In the late 1980's, we have witnessed an increasing concern about our global commons and long-range transboundary transport of pollutants including acid rain, carbon dioxide and the greenhouse gases, chlorofluorocarbons and ozone depletion of the stratosphere. No new legislation has been passed, but we may be nearing landmark acts as public sentiment, chance events, and research results coalesce to form a national consensus. What distinguishes our generation from previous generations throughout history is not our negative effect on the environment, but rather the magnitude of that effect. We are impacting larger and larger domains: groundwater aquifers, not just surface waters; oceans, not just coastal waters; the stratosphere, not just urban air. In industrialized nations, our anthropogenic energy flux per unit area exceeds that of photosynthesis by about a factor of ten (1).

It is the purpose of this paper to discuss these environmental problems and research needs, both basic and applied, as they affect water quality. What are the current and future environmental problems and what should be our research strategies to address those problems?

Research Goals

My own future research goals are in three main areas: 1) assessing aquatic effects of acid rain; 2) modeling effects due to climate alteration and ozone depletion; and 3) groundwater pesticide modeling and risk assessment.

Aquatic effects of acid rain have been studied intensively since 1980 under the 10-year National Acid Precipitation Assessment Program (NAPAP). The Program is in its final throws after a controversial interim report that was criticized by Congress. I fully expect new acid rain (and precursor air pollutant) legislation to be passed under either a Democratic or Republican administration. NAPAP is a large program ($86 million in 1987) which has curtailed funding of other environmental research by EPA, USDA, NOAA, DOE, DOI, and TVA since the mid-1980's. Other research programs are already jockeying for position to take over acid rain research funds. From my perspective, there is still a lot to be accomplished before NAPAP funding wanes in 1990.

Mathematical models of aquatic effects of acid rain (mainly chemical effects) have been funded by EPA and the Electric Power Research Institute (EPRI). These models have been calibrated with data from 10-20 gaged watersheds in the US, Norway, and Canada. But the models have not really been validated with laboratory and field manipulations, and such experiments need to be performed to complete the acid rain story. That is: acidification of lakes has occurred in sensitive hydrologic and geologic settings due to acid rain; it has affected approximately 1000-2000 lakes in the eastern half of North America, generally small lakes less than 50 hectares; it is largely reversible, especially the chemical effects, and will respond on the order of a few hydraulic detention times in most cases; few additional lakes will become acidic under present levels of acid deposition, but acidification pulses during snowmelt and storm events are problematic for streams and fisheries; effects of other associated pollutants in precipitation (Hg, Pb, Cd, Zn, toxic organics) may be heightened by acidification.

Professor Rich Valentine and I are trying to use laboratory and field results with surface chemistry theory to improve the reliability of models for decision making (Figure 1). Imbedded in this work is the notion that the modeler benefits greatly from planning and performing experiments directly related to model development. Ideally, reproducible experiments should be performed on a small and simple scale in the laboratory, and field experiments should be carried out in small plots, stream channels, or whole watersheds for added realism. Often both are necessary to understand complex environmental systems. Figure 1 shows the twin streams (Bear Brooks) at Lead Mountain, Maine, the site of experimental acidification to test acid rain models.

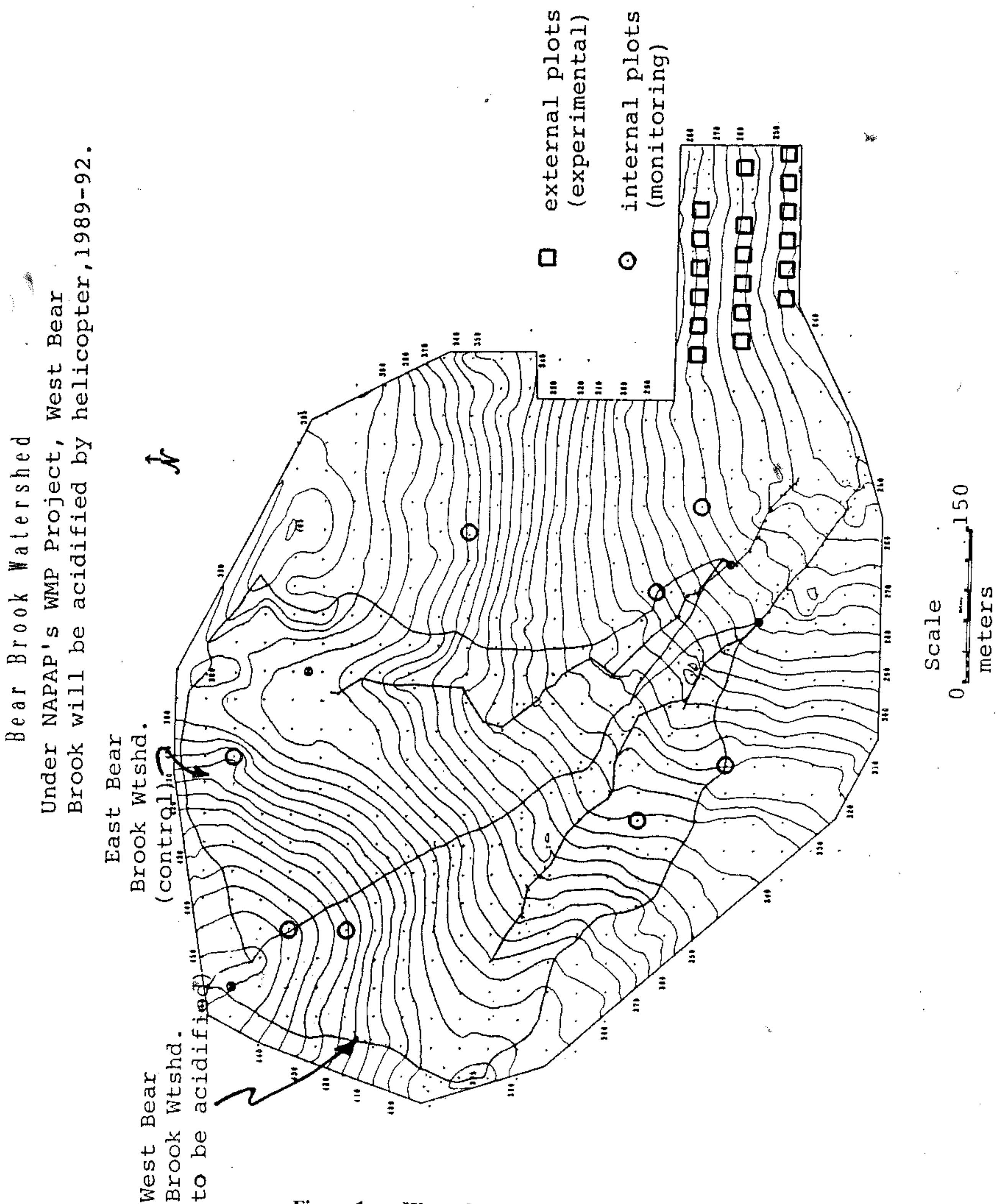

Figure 1: **Watershed Manipulation Project**

All model predictions (mean or expected values) should be accompanied by an estimate of uncertainty (standard deviation or second moment). In the future, decision makers will want to know the "best estimate" as well as the certainty of the prediction. Thus, we are including first-order second moment uncertainty analyses or Monte Carlo simulations with all water quality models (Figure 2). Professor Konstantine Georgakakos and I hope to extend our acid rain model (ETD Model) (2-4) to aquatic and terrestrial ecological effects due to climate alteration and ozone depletion using the National Surface Water Survey and Eastern Soil Survey (5).

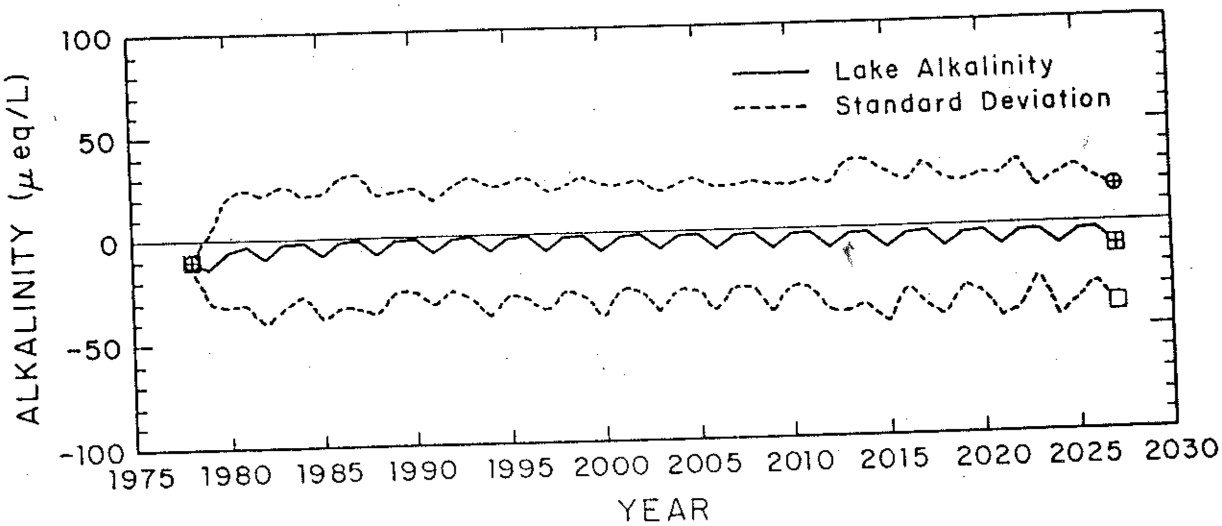

Figure 2: **Result of 50-year Simulation for Woods Lake, New York, in the Adirondack Mountains. The middle line is the expected value of alkalinity simulation and the outside lines are ± 1 standard deviation from first order second moment uncertainty analysis.**

At The University of Iowa, we have formed a new Center for Health Effects of Environmental Contamination (CHEEC), of which Professor Gene Parkin is Director. It is an interdisciplinary research team from the Departments of Civil and Environmental Engineering, Preventive Medicine and Environmental Health, Pediatrics, Pathology, Urban and Regional Planning, Geology, and the University Hygienic Laboratory. It was initiated by the Iowa Groundwater Protection Act of 1987, a novel approach to groundwater problems relying on pesticide taxes, education, demonstration, and research to improve the State's groundwater quality (rather than regulations). We have used this Center as a vehicle for groundwater research, especially exposure assessment modeling, monitoring, and biotransformation research. Gene and I are interested in the role of electron acceptors (dissolved oxygen, nitrate, sulfate and carbon dioxide) on biotransformation kinetics, and we are designing riparian zone buffer strips for nutrient and pesticide removal before percolation and runoff to groundwater and streams. Professor Burt Kross is in charge of two studies under CHEEC and the National Pesticide Survey for groundwater monitoring of pesticide contamination in well waters. In general, pesticide concentrations in shallow wells are less than stream concentrations, but they seem to be on the rise with increasing applications of soluble herbicides.

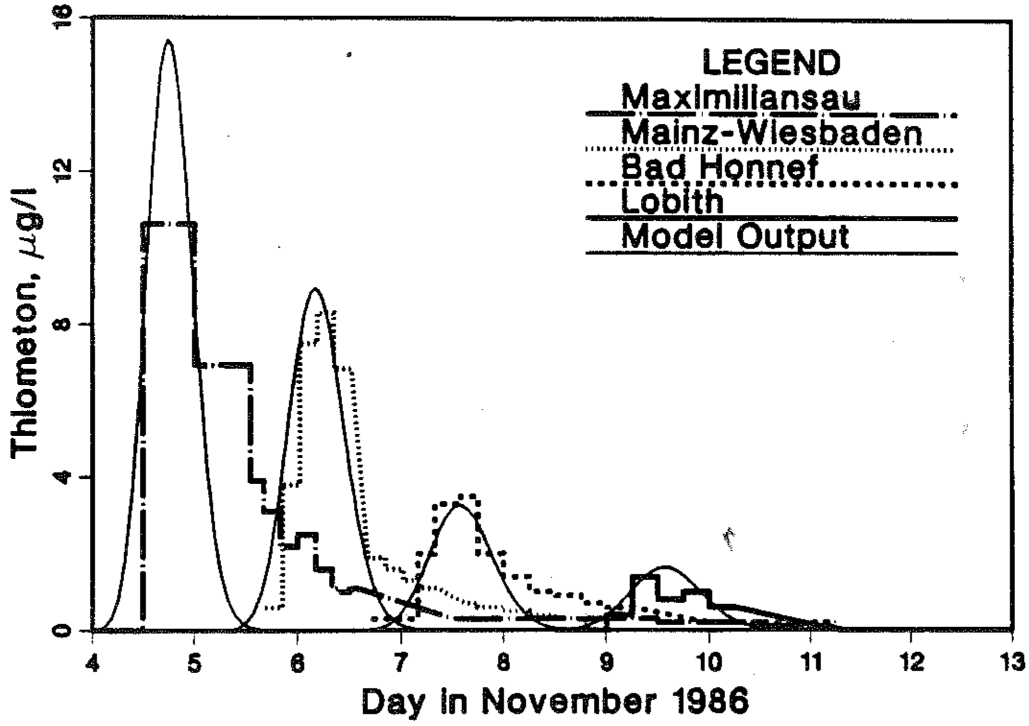

Figure 3: **Field Measurements and Model Results Following the Chemical Spill at Basel, Switzerland. Dashed lines represent field measurements at four downstream stations, Karlsruhe, Mainz, Bad Honnef, and Lobith. Model results are the solid lines.**

Lastly, one of our dreams is to assemble an emergency response team for chemical spills, not for remediation (those procedures already exist), but for verification of mathematical models. The number of chemical spills each year (2237 reported in 1987 in Pennsylvania, Illinois, Ohio, Texas and California) represents tremendous information lost to modelers because requisite data was not collected on mass discharge amounts, concentrations, and related parameters (nitrate induced photolysis, light penetration, dissolved oxygen, pH, bacterial population, temperature, etc.). Experience with the Rhine River chemical spill at Basel, Switzerland, in November of 1986, indicated that just a few mass discharge measurements at the outfall would have greatly improved the data set for model validation. Nevertheless, a relatively good record of the spill was obtained by German authorities that increased our confidence in toxic chemical transformation kinetics and plug-flow-with-dispersion transport models (Figure 3) (6-8). The goal is to build better models for decision making, and it is an iterative process that absolutely requires testing at every level.

Environmental Problems

How does one rank order problems in terms of their impact on the environment? Recent surveys of our students in the Environmental Engineering Program show that the answer is dependent on how the question is phrased, and properly so. If you ask the students to rank environmental problems in terms of their present effect on human health in the world, inevitably, waterborne disease (e.g., dysentery) and sanitation are the most frequent answers. If you ask the question in terms of ecological health of the world, you receive answers of deforestation, habitat destruction, and species extinction.

In February of 1988, I participated in a workshop for EPA on a "Longterm Research Plan for Ecological Resources: Surface Waters". We were asked to rank the environmental problems that cause the greatest ecological change in the U.S. based on areal extent of damage (e.g., miles of streams, hectares of lakes). The workshop proposed the following list, in rank order.

- Habitat Destruction
- Eutrophication
- Toxic Chemicals
- Global Climate/Ozone Depletion

The Workshop felt justified, but uneasy, with the above list because the top two items, habitat destruction and eutrophication, do not generate excitement these days in the United States. Although a strong case can be made that soil erosion, sedimentation, navigation, dredging, cultural development and wetlands destruction account for most ecological damage in the U.S., toxic chemicals receive the most public attention, probably due to potential human health effects. In the final analysis, human health will always play an important role in determining research funding. Issues of global climate change (greenhouse gases) and stratospheric ozone depletion were thought to have the greatest potential for human and ecological damage but also the most uncertainty.

Given such uncertainties, a multiphase/multi-media outlook is desirable to discuss future environmental problems. Let us divide it into three classes of problems (not in rank order): 1) Air/Water Interface; 2) Land/Water Interface; and 3) Water Quality.

Air/Water Interface

At the air/water interface, there are four classes of pollutants that will play a part in future environmental problems.

- Acid Deposition (sulfuric, nitric, hydrochloric)
- Photochemical Oxidants (ozone, H_2O_2, radicals)
- Organic Air Pollutants (hydrocarbons, SARA 313 emissions)
- Heavy Metals Deposition (Hg, Pb, Cd, Zn)

Both wet and dry deposition of acids will continue to be a problem, but new legislation should help to control sulfur oxides at least. If we change from landfilling to incineration of municipal solid waste, we may expect greater concentrations of HCl in urban fog and water due to plastics combustion, based on the European experience (9). Dry deposition is very important, and research will be needed to better measure dry deposition of many pollutants in fogs, gases, and aerosol particles. Atmospheric deposition of nitric acid (nitrate) is an increasingly large problem in eutrophication of N-limited coastal waters. Estimates by the Environmental Defense Fund place the percentage of nitrogen inputs from wet and dry nitrate atmospheric deposition at 25 percent of the total inputs (point and nonpoint) to Chesapeake Bay (10). Although the runoff of nitrate from acid rain in the catchment area of Chesapeake Bay is probably overestimated, the EDF Report demonstrates a surprising atmospheric pathway of fertilization for a large estuary in an urban setting.

Oxidant research is needed at both the air/water interface and the air/canopy interface to assess crop damage, smog, and forest effects. Atmospheric aqueous phase reaction sequences (cloud water reactions) will be needed to distinguish between superoxide (O_2^-) and hydroxyl radicals ($\cdot OH$) as oxidants in the homogeneous aqueous phase, together with ozone and hydrogen peroxide. Fog waters, with ion strengths as high as 0.1 M and pH values as low as 2.0, should be a central focus of forest and crop foliar effects research, where oxidants and heavy metals are implicated. Heterogeneous reactions, including metal catalysts and photoreduction of Fe(III) in atmospheric and surface waters, may play an important role in cycles governing photochemical oxidation reactions. The question of linearity between emissions and deposition for the pollutants of the photochemical cycle NO_x-SO_x-HC-O_3 will remain central to the issue of further emission controls in urban (and regional) air pollution problems. There is mounting evidence that hydrocarbon emissions from mobile sources may need to be reduced in order to affect reductions in sulfate or nitrate in acid deposition.

Organic chemicals at the air/water interface include hydrocarbons and other organics from fugitive and stack emissions. The Superfund Amendments and Reauthorization Act of 1986 (SARA), under Title III and Section 313, provided for public notification (right-to-know) of toxics on a list of some 300 chemicals. SARA 313 was a response to the methylisocyanate release and disaster at Bhopal, India. It is landmark legislation because, for the first time, industries must monitor and estimate emissions of specific organic chemicals in air and water effluents that were heretofore unmeasured and not requiring a permit. Enormously sobering is the list that citizens will eventually receive detailing emissions of an estimated 50 million pounds per year of toxic chemicals. The concept of "right-to-know" is appropriate in a free and democratic society, but I believe the most important result of the legislation will be the reduction in emissions achieved by industry once industry concentrates on decreasing the amounts of chemicals on its lists. In that respect, it may be the most important piece of air pollution legislation since the 1977 Clean Air Act Amendments. The great majority of organic chemical emissions are to the atmosphere, so local and regional air models of specific organic pollutants may be needed with a coincident emphasis on atmospheric gas-phase reactions and research. We will try to answer the deceptively simple question, "Where do all the chemicals go?"

Heavy metals, especially the volatile metals (Hg, Pb, Cd, Zn) present at the air/water interface, are a potential problem from the standpoint of ecological effects on forests, crops, and atmospheric deposition to surface waters. Low alkalinity lakes in the Upper Midwest and Canada are especially susceptible to mercury bioaccumulation in fish. There are more lakes closed to fishing in Sweden and Canada due to mercury contamination than the loss of fishing due to acidification. The exact mechanism between low pH and mercury bioaccumulation is still unknown. It bioaccumulates in fish to levels in excess of the FDA "action limit" of 1 mg/kg from concentrations as low as 50 ng/L. On the brighter side, there have been widespread decreases in lead concentrations in streams since 1979 in the US, probably due to the five-fold decrease in lead consumption for gasoline. Unfortunately, along with the decreases in lead have been significant increases in nitrate, arsenic and cadmium (11). It is not advisable to drink water from a rain barrel any longer in urban airsheds. A recent survey of heavy metals in precipitation in Kentucky and Tennessee measured average concentrations of Cd, Cu, and Pb of 0.44, 19, and 73 µg/L, respectively, with lead in violation of drinking water standards even before leaching of plumbing fixtures (12)!

Land/Water Interface

At the land/water interface, there are several recent or emerging environmental problems.

- Groundwater Contamination
- Agricultural Runoff
- Landfill/Dumpsite Remediation
- Specialty Problems

These issues are interrelated. Groundwater contamination is caused by landfill leachate, chemical spills, and toxic chemical dump sites, as well as agricultural fertilizer and pesticide infiltration. They are all nonpoint source problems. In the US, progress has been made on point source controls of municipal and industrial wastewater, but improvements in nonpoint source control is more difficult and costly. Imagine the cost of disposing of 10 million kilograms of extremely toxic chemicals in a hazardous waste landfill or by incineration. Yet that is the amount of pesticides that is placed freely on the soil over Iowa each year! Research trends indicate that we can expect lower pesticide application rates via novel delivery systems (such as microencapsulation) and genetically-engineered plants that are tolerant to the most effective pesticides.

Landfills and dumpsites will continue to leak and generate toxic chemical inputs to surface water and groundwater. Remediation at 951 sites on the National Priorities List (NPL) for Superfund is going slowly; only 24 sites have been completely cleared at a cost of $20-30 million each. But such figures are somewhat misleading. Actually, considerable action has occurred as noted in the following (13):

818 - Removal Actions at non-NPL sites
264 - Removal Actions at NPL sites
472 - Remedial Investigation/Feasibility Studies
106 - Remedial Designs undertaken
65 - Remedial Actions in progress
24 - Remedial Actions completed (O & M now)

Hopefully, by the year 2010 or so, we will have cleaned-up the historical Superfund sites, and our rate of generating new sites should have greatly diminished. Municipal landfill leachates also are quite toxic, so the long term regulatory trend must be towards recycle, reuse, energy recovery and incineration.

EPA's Innovative Technology program is a good example of a program that has stimulated research in areas of in-situ bioreclamation, incineration, and solidification of wastes. More upstream research is needed.

Specialty problems at the land/water interface include potential release of genetically-engineered microorganisms to the environment, disposal of infectious wastes, radioactive wastes, and agricultural return flows. Mining waste leachates and agricultural return flows (e.g., Kesterson Reservoir in the central valley of California) loom as very large and difficult problems in the western United States. In fact, shortages of water in the Southwest will cause water recycling and reuse to come by necessity in the 21st century and at great cost!

Water Quality, Ecological Health, Human Health

Protection of water quality in the United States has depended, in part, on scientifically-defensible water quality criteria since 1972. Research in water quality criteria and toxicity evaluations is still primitive as it relates to the structure and function of real ecosystems and, even more so, to human health. We need site-specific water quality criteria and standards that take into account the toxicity of individual chemical species at a given site with the chemistry of complexing ligands fully considered, presuming our ability to measure and predict chemical speciation. Secondly, we need water quality criteria, modeling and toxicity evaluations of in-place pollutants, especially contaminated sediments, which are responsible for closed fisheries at a number of major water resources (PCBs in the Great Lakes and Hudson River, dioxin and heavy metals contamination of several large rivers). Thirdly, we need a better way of coping with multiple pollutant, multiple biological species problems in order to assure biological integrity of our nation's waters and yet not regulate industrial activity unnecessarily. New chemicals are being manufactured at a rate of 700-1500 per year. We must ask ourselves, "Do we know enough about the status of our ecosystem to determine subtle ecological changes?"

Most fish kills and gross changes in species diversity and community status are caused by oxygen depletion, habitat alteration, eutrophication and red tides. Chemical spills also contribute to fish kills on an event basis. But can we distinguish slow ecological changes? Is the ecological health of our nation's surface waters getting better or worse? I don't think we know. It is for that reason that we will need an Ecological Inventory for a baseline of our surface waters over the next five years. It should not be solely a catalog of species and densities, but rather it should include a strong research component of long term ecosystem studies, large scale experimental manipulations, establishment of structure-function relationships, and ecological modeling.

As for human health, the linkages between water quality and disease are tenuous, at best. Our drinking water standards are sorely in need of revision, but the process is already in place and 85 MCLs will be added by 1990 under the Safe Drinking Water Act Amendments. Quantitative risk assessments are the chosen method for evaluation of human health risk, but there is little sound scientific basis for it (14). Extrapolation from animal bioassays to humans is difficult, especially from tests done at high doses to effects on humans at low doses (such as the linear multistage model, LMM, for dose-response). Exposure assessment and exposure modeling is also difficult. Monitoring data for exposure of humans to toxicants is sparse, and data sets for calibration/verification of exposure models is almost nonexistent. Recently, the high priority given to water pollution has been questioned relative to risks posed by natural toxins (e.g., aflatoxin from fungus mold) and other factors (diet, viral agents, and genetic predisposition). Bruce Ames, Chairman of Biochemistry at UC-Berkeley concludes, "This ranking suggests that carcinogenic hazards from current levels of pesticide residues or water pollution are likely to be of *minimal concern* relative to background levels of natural substances..." (14) (emphasis added).

There is a huge uncertainty in risk assessment and risk management. The traditional methodology of EPA (hazard identification, dose-response assessment, exposure assessment, and risk characterization) (15) involves a series of conservative assumptions that may be more than prudent. Application of similar methodologies among agencies for recent dioxin (2,3,7,8-tetrachloro-dibenzo-dioxin) risk assessments have resulted in gross differences of allowable intakes: 2000-fold (Table 1).

TABLE 1: Dioxin Risk Assessment

Results were from four different agencies using the linear multistage model and the safety factor approach for dose-response and assume a 10^{-6} allowable cancer risk over a 70 year lifetime exposure.

Agency	Effect	Method	Allowable Intake femtograms/kg-day
EPA	Liver Cancer	LMM	6.4-100
CDC	Liver Cancer	LMM	28-1428
FDA	Liver Cancer	SF-77*	13,000
California	Liver Cancer	LMM	7.4

*NOAEL 0.001 µg/kg-day

Radon is an example of a naturally-occurring hazard that is relatively quite risky as a carcinogen. Average concentrations of radon gas in indoor air are about 50 Becquerels per cubic meter (1.4 picocuries per liter) which corresponds to a cancer risk of 1-in-250 or 0.4 percent. Radon would account for approximately

10,000 lung cancer deaths per year (16). It is less than the risk of death due to automobile accidents (2.0 percent risk) but more than all ambient outdoor air pollutants and even occupational exposures at chemical plants! At the highest exposure levels measured in homes, risks due to radon are commensurate with cigarette smoking (30 percent risk), yet the vast majority of lung cancers are related to smoking. It is likely that most of the increased risk of lung cancer due to radon exposure is in smokers (17).

Given all the uncertainties in risk assessment, it should be mentioned that sometimes a management decision must be made in the absence of solid scientific evidence. When EPA made the decision to eliminate lead from gasoline in 1972, it was a very costly decision to industry and society (every car needed a catalytic converter; gasoline refining costs increased). Human health data on effects of lead exposure were extremely thin. Yet the decision was made, and it has proven to be excellent in view of more recent data on neurological effects, brain development, and carcinogenicity of lead. Japan, Europe, and other countries have followed our example. Despite all the uncertainties, we must set priorities and act where it is prudent. Human health effects from environmental exposure have been demonstrated for lead, mercury, asbestos, sulfur dioxide, ozone, and formaldehyde. Worker exposure and effects have been demonstrated for a host of pollutants including lead, arsenic, mercury, cadmium, vinyl chloride, asbestos, benzene, and others. The good news is that human life expectancy is increasing, and cancer rates are not increasing but have been steady for 50 years in the United States (14). There have been documented health effects from environmental exposure, though it usually has been due to air pollution, water borne infectious disease, or heavy metals (Minimata Bay).

To summarize environmental problems, I propose the following list, in rank order of importance and/or urgency.

1. Air Pollution and the Air/Water Interface
    - global climate changes
    - stratospheric ozone
    - photochemical oxidants
    - acid rain
    - SARA 313 emissions
2. Ecological Health and Habitat Destruction - Water
    - wetlands destruction (species extinction)
    - soil erosion and sedimentation
    - coastal zone pollution (anoxia, eutrophication, wastes)
    - ecotoxicology and ecological inventory
3. Water Pollution
    - agriculture runoff (metals, nutrients, pesticides)
    - groundwater pollution (organics, pesticides)
    - water quality criteria (organics, metals)
    - reuse and recycling

Research Needs

Research is required to address these environmental problems. In particular, we seek answers to the following questions:

- Where do all the chemicals go? Fate Modeling

- What are their effects (ecological and human)? Effects
- How do we clean them up? Engineering Technology
- How clean is clean? Risk Assessment/Management

For the first question, we invoke environmental science and fate modeling. Needed is knowledge on the various fate and transport processes in the environment including advection, dispersion, phototransformations, chemical hydrolysis, redox reactions, sorption/desorption, bioconcentration, volatilization/gas transfer, and biological transformation. In recent years, excellent progress has been made on most of the fate and transport processes. Given just three chemical parameters: octanol/water partition coefficient, Henry's constant (vapor pressure and solubility) and absorption spectra, one can predict approximate rate constants for all of the pathways except biotransformation for most organic chemicals. Heavy metals are more difficult due to their many chemical species, redox reactions, and sorption to surfaces. Given the list of environmental problems, we might focus our research priorities on photochemistry, aquatic surface chemistry, and biotransformation.

Aquatic surface chemistry and surface complexation holds the secret for understanding many environmental processes including heavy metals mobility and sorption to solid phases, corrosion, chemical weathering in watersheds receiving acid deposition, coagulation in natural waters, chemical precipitation and formation of solid solutions, and heterogeneous catalysis. Photochemistry will help to unlock puzzles at the air/water interface and for oxidant/radical transformation reactions. Biological transformations are the most important fate process in natural water and wastewater treatment. Better theory is needed to predict biological degradation reactions and their rate constants. Quantitative structure activity relationships may be developed, at least for classes of compounds, as a function of oxidant (electron acceptor).

If an ecological census is to be made over the next five years, it should have a large component of ecotoxicology and research included. We need to understand not only how many organisms are present, but how they are interdependent and why they are present or absent. A biological inventory alone runs the risk of being lost in annual and spatial variability without increases in understanding. The census should include research on water quality criteria and in-place pollutants.

In environmental engineering, new treatment technologies must be developed for old problems (municipal wastewater) as well as new problems (remediation of contaminated groundwater sites). Our field is given a surge each time that a new problem emerges -- it is easier to be creative on a new problem. We suffer as a field from being limited to the same feedstock (wastewater) or raw material (water). New problems will likely involve groundwater remediation, landfill alternatives, air pollution control, and genetically engineered microorganisms. Problems pose new possibilities and opportunities.

Exposure assessment and mathematical modeling is needed to address the uncertainty in environmental predictions and risk assessments. It is a tool that will be used increasingly as the cost of computing rapidly approaches zero and with development of expert systems software. Despite temptations, it should be used only in conjunction with model testing at the laboratory pilot, and field scale. An emergency response team could develop a plan for validating models at spill sites. In this way, the environmental engineer can and should participate in risk management, environmental policy alternatives and decision-making. To summarize our research needs:

- Aquatic Surface Chemistry
- Environmental Photochemistry
- Biological Transformations
- Ecotoxicology (inventory & criteria)

- Engineering Technology
- Exposure Assessment Modeling
- Risk Assessment/Management

Summary

In this paper, environmental problems and research needs have been discussed. It remains to be seen how to solve those problems and satisfy research needs. It will take cooperation of all parties, including industry, EPA, NSF and universities. The best model for university-government-industry cooperation is the recent project on stratospheric ozone between universities, NASA, and CMA-DuPont. It was funded by CMA and NASA. Because DuPont and the chemical industry were intimately involved in the research from the beginning, they were in full agreement with the finding that chlorofluorocarbons (CFCs) do, indeed, contribute to ozone depletion over Antarctica. They have voluntarily planned to curtail production of all CFCs by 1992. A side benefit for industry was the early warning to plan for substitute chemical manufacturing.

Our adversarial system has served us well to this point, but litigation makes environmental controls ever more difficult to implement and enforce. As an alternative, Clean Sites Incorporated has served well as a role model in mediating among Superfund responsible parties. It is time to search for new paradigms of university-government-industry cooperation. Perhaps AEEP and the environmental engineering profession can play a central role bringing together all parties at the research stage to solve some of the regulatory and environmental problems.

References

1. Stumm, Werner (1986). Water, an Endangered Ecosystem. *Ambio* 15:4, 201-07.

2. Lin, J.C. and Schnoor, J.L. (1986). Acid Precipitation Model for Seepage Lakes. *Journal of Environmental Engineering* 112:4, 677-94.

3. Nikolaidis, N.P. et al. (1988). A Generalized Software Acidification Model for Lakes. *Water Resources Research* (in press).

4. Nikolaidis, N.P. et al. (1988). Verification and Long Term Simulations of an Acid Precipitation Model for the Northeastern U.S. *Journal Water Pollution Control Federation* (in press).

5. Linthurst, R.A. et al. (1986). Characteristics of Lakes in the Eastern United States, Vol. 1. USEPA, 600/4-86/007A.

6. Reichert, P. and Wanner, O. (1987). Simulation of a Severe Case of Pollution of the Rhine River. Proceedings of the XXII IAHR Congress, Technical Session A, Lausanne, Switzerland, 239-244.

7. Capel, P.D., Giger, W., Reichert, P. and Wanner, O. (1988). Accidental Input of Pesticides into the Rhine River. *Environ. Sci. and Technol.*, (in press).

8. Mossman, D.B., Schnoor, J.L. and Stumm, W. (1988). Predicting the Effects of a Pesticide Release to the Rhine River. *Journal Water Pollution Control Federation* (in press).

9. Stumm, W., Sigg, L., and Schnoor, J.L. (1987). Aquatic Chemistry of Acid Deposition. *Environ. Sci. Technol.* 21:1,8-13.

10. Goffman, J. (1988). Testimony before the Subcommittee on Natural Resources, Agriculture Research and Environment of the Committee on Science, Space and Technology, House of Representatives (April 27, 1988), Environmental Defense Fund, Washington, D.C.

11. Smith, R.A., Alexander, R.B. and Wolman, M.G. (1987). Water Quality Trends in the Nation's Rivers. *Science*, 235, 1607-15.

12. Olem, Harvey (1988). Personal correspondence, Tennessee Valley Authority.

13. Clean Sites Incorporated (1988). Clean Sites - 1987, Alexandria, Virginia, 15 pp.

14. Ames, B.N., Magaw, R. and Gold, L.S. (198). Ranking Possible Carcinogenic Hazards. *Science*, 236, 271-80.

15. Russell, M. and Gruber, M. (1987). Risk Assessment in Environmental Policy-Making. *Science*, 236, 286-90.

16. Nero, A.V., Jr. (1988). Controlling Indoor Air Pollution. *Scientific American*, 258:5, 24-30.

17. Krieger, J. (1988). Study Revises Cancer Risk from Radon. *Chemical & Engineering News*, January 18, 22.

Discussion: Environmental Research Strategies for Multiphase Systems - Water

Christine A. Shoemaker
School of Civil and Environmental Engineering
Cornell University
Ithaca, New York 14850

I do agree with Professor Schnoor on most of his points including the importance of research on aquatic surface chemistry, biotransformation, uncertainty in model predictions, the role of temporal and spatial variability in assessing the ecological impact of pollution, and risk assessment. He has discussed a wide range of issues in his paper. Because of space and time limitations, I will discuss issues only from the four topics listed below, followed by a proposal for encouraging the interdisciplinary research necessary to address these problems.

Uncertainty in Model Output

Professor Schnoor has identified the need to quantify the uncertainty associated with output from models of environmental processes. He mentions two methods that can be used to estimate uncertainty associated with descriptive simulation models. In addition to these techniques, I would add the class of methods referred to as "parameter identification." Such methods are designed to utilize simultaneous measurements on many components of a system. Hence information about system interaction is used in obtaining better estimates than would be possible by looking only at measurements of individual components.

One area related to parameter identification is the use of statistically based procedures for determining the location and magnitude of sources of pollution based on data collected in areas where there are many potential sources. Direct areas of application of these methods include the establishment of responsibility for groundwater contamination and remediation and for identifying industries whose air emissions should be reduced.

We also require more research on the methodology associated with model validation. There are many ad hoc methods by which researchers attempt to evaluate the reliability of their models, but there is a need for a more rigorous, statistically based methodology that incorporates a) the type of application -- (e.g. management or investigation of basic processes) for which the model is designed; and b) the quality of data available for calibration and validation. Such a methodology should include the flexibility to update model parameters and reliability estimates as new monitoring data become available.

Fate and Transport

I am not as optimistic as Professor Schoor about our ability to predict fate and transport of organic chemicals in the subsurface environment. In particular, vapor phase sorption is poorly understood and is potentially very important in relatively dry unsaturated regions in the subsurface. Peterson et al. (1988) report vapor phase sorption coefficients that are orders of magnitude higher than those determined under saturated conditions. Modelling analysis (Peterson et al., 1988, Shoemaker et al., in preparation) indicates that ignoring vapor phase sorption, as is typically done in modelling studies, results in a significant overestimation of the speed and amount of transport of volatile organic materials into groundwater.

Biological transformation is also an area that is certainly important, but I do not agree with Professor Schnoor that it is necessarily the "most important fate process". Our ability to restore water quality and to prevent environmental contamination will require an *integrated* quantitative analysis of the interaction between transport, phase transformation, and biodegradation through a combination of experimental and modelling studies. For example, groundwater contaminants that are soluble with low sorption coefficients may move through the unsaturated soil so quickly that little biodegradation has time to occur. Hence the importance of biodegradation depends not only on the vigor and density of the degrading organisms but also upon physical and chemical processes on which the organisms may have little effect.

Use of Models in Management

Professor Schnoor has discussed the use of models for making management decisions, but has not discussed the components of these models or the methodology required to solve them. Such models should include a description of the economic cost and the environmental impact of alternative strategies for controlling multi-phase pollution problems. There has been a fair amount of work on fate and transport modelling, but much less associated with management models that incorporate a description of the specific management options and their economic cost and environmental impact. Research issues include a) the development of optimization methods to select the best alternatives, b) appropriate ways to quantify both the economic cost and its stochasticity, and c) developing an adequate description of the levels of risk one is willing to tolerate. These procedures can be very complex computationally, and it is important that research in this area consider computational efficiency and the rapid change in computing power that will continue over the next decade. Optimization methods used in conjunction with models that incorporate economic costs, quantification of acceptable risk, and reliable descriptions of fate and transport can suggest management options that potentially can save millions of dollars.

Priorities

In contrast to Professor Schnoor, I would list groundwater contamination and source control as top priorities under the water quality category, where "source control" includes the pretreatment of waste products, the change in commercial, industrial and agricultural processes to reduce the production of toxic waste products, and the development of techniques (such as improved landfill design) to reduce the movement of disposed waste into the environment. An additional top priority area is the integration of economic analysis and management modelling with detailed descriptions of fate and transport of multi-phase pollutants in order to develop cost-effective solutions to environmental problems. I would not rank "agricultural runoff" as highly as these other problems since the amount of pesticide leaving a crop field by runoff is typically much less than that transported by air-borne drift or by subsurface transport. Non-agricultural sources of runoff are often as significant as agricultural runoff.

Encouraging Interdisciplinary Research

For many of the types of problems Professor Schnoor and I have discussed, it is necessary to have input from engineers and scientists with a range of backgrounds. It has been my experience that some of the most successful interdisciplinary research is done by groups of between two and five investigators and their students or assistants. The current NSF structure is designed to evaluate either single investigator projects or the larger group projects associated with the Research Centers. It is of course true that multiple investigator grants are funded under the normal granting procedure, but the budgets associated with such grants are usually not much larger than those given to single investigators. Hence investigators are encouraged to submit their own independent proposals rather than to develop an integrated multi-investigator project. The number of Research Centers that will be established to deal with environmental problems is expected to be very small, and hence the Research Center program will probably not have a widespread effect on environmental research.

I suggest that we would make faster progress on the interdisciplinary aspects of environmental research if a mechanism or understanding were established that projects from several multiple investigators could be funded at levels that are approximately equal to the sum total of individual project proposals. An alternative would be to develop a formal mechanisms by which several related proposals could be judged independently but also evaluated in terms of each of their contributions to a co-ordinated effort.

Summary

I am in general agreement with Professor Schnoor's points, but I would put more emphasis on experimental and modelling studies of the interaction between physical, chemical and biological transformations (rather than just focusing on biological transformation) and on the modelling methodology (optimization methods, parameter identification, and statistical validation procedures) required to develop models that are useful to understand and manage multi-phase contamination problems. I also think that significant attention should be paid to source control of pollutants, but I acknowledge that many of these types of studies are perhaps best located in divisions of NSF other than Environmental Engineering since the focus of source control is often on a particular industrial practice. Lastly, I would encourage NSF to develop a funding mechanism that encourages co-operative research among several (two to five) investigators.

References

Peterson, M.S., L.W. Lion, and C.A. Shoemaker (1988) Influence of Vapor-Phase Sorption and Diffusion on the Fate of Trichloroethylene in an Unsaturated Aquifer System, *Envir. Sci. and Tech.*, 22, 571-578.

Forward-Looking and Backward-Looking Views of Uncertainty

Talbot Page
Center for Environmental Studies
Brown University
Providence, Rhode Island 02912

Introduction

How do we think, and how should we think, about uncertainty? The purpose of this note is, by addressing these two questions, to set a context for some current research and then to briefly describe this work. The two questions -- how do we and how should we think about uncertainty -- are obviously important in any science, but they are particularly important in environmental science and engineering. In the environmental area uncertainties are often especially large, yet many times decisions must be made, using the current limited information and understanding (decisions to postpone action are just as much decisions as decisions to take precautionary action). Often the stakes are high and relatively irreversible, so that it is important to get the right balance of risk taking and precautionary action at each step of sequential decision making.

The current situation seems to be as follows: compared with (say) a hundred years ago we are much more sophisticated formally, as statistics and probability theory have blossomed; we still have a good deal of trouble thinking about uncertainty substantively; but there have been some developments in the past several years that offer some fresh vantage points and opportunities in the ways we think about uncertainty.

I will briefly identify what appear to me a few of these vantage points which Richard McKelvey and I are exploring in our current research.

How Should We Think About Uncertainty?

I will start with more settled matters and move toward the less settled. First, when we make quantitative estimates, it is clear that these estimates have little meaning unless they are accompanied with judgments of their uncertainty (or equivalently "precision"). The large literature of classical statistics helps us assess measurement uncertainty (error) in quantative terms, using probability language (standard deviations, etc.). I take it as an uncontroversial starting point that we should assess measurement uncertainty probabilistically.

Second, when we make quantitative estimates there is also the possibility of systematic error. Calculations are based on models, and some of the modelling assumptions may themselves be associated with varying degrees of uncertainty. I think it is widely agreed that we should attempt to assess systematic error (uncertainty associated with models), but there seems to be some uncertainty -- if I can put it that way -- over just how we should do this. In evaluating estimates of physical constants such as the speed of light, physicists constructed a Birge index which combined assessment of systematic and measurement error. Applied more often, the statistics literature on hypothesis testing helps us assess systematic uncertainty in quantitative and probabilistic terms.

But to some decision theorists the literature on hypothesis testing is not fully satisfactory because it focuses on the question "conditioned on there being no effect (and the underlying model being true), what is the probability of the experimental result, or one more extreme?" This is the question of significance levels and p-values. The more important question for decision purposes is "conditioned on the experimental result, what is the probability that there is an effect?" Inverting the conditional this way leads to a more explicit and quantitative assessment of systematic uncertainty.

Third, as just anticipated, we are often uncertain about some facts or <u>state of nature</u>. We might be uncertain as to whether viruses can infiltrate to groundwater aquifers, a chemical is a carcinogen, or ozone depletion is caused (at a particular level) by CFCs. My old teacher, Jack Kiefer, would point out that these last examples are not examples of repeatable events, and he would conclude that probability language is not appropriate for unique events. He would say, dismissively, that the probability that a particular chemical is a carcinogen is either zero or one, but he didn't know which.

While I realize that this is an unsettled matter, I have come to view that uncertainties for such unique events should be expressed quantitatively and in probability language. In saying this, I agree that even aside from the normative issue of appropriateness, it is simply hard to develop a reasoned basis for making probability judgments about unique events. Without practice and development of skill it often feels that such probability numbers are "pulled out of the air" (and even with practice it sometimes still feels that way). Still, I think there are several reasons for investigating how people form judgmental probabilities and encouraging scientists to use them, especially for unique events such as the carcinogenicity of a chemical.

First, probability language provides a bridge of communication between technical people who do the science and live with the uncertainties of their investigations and the policy people who make decisions based on information provided by others. For example, Hoare undertook an epidemiological study of 2,4-D and non-Hogkin's lymphoma which came out statistically significant at an odds ratio of about 5:1. The paper discussed at length various sources of systematic error which might undermine the result. While this part of the paper was the most interesting to me, the discussion here was qualitative and I could not tell how seriously she took the various modelling uncertainties. So I asked her what probability she attached to 2, 4-D being a carcinogen (causing non-Hogkin's lymphoma with odds ratio of 5:1 or more).

She told me that in her judgment there was about an 80 percent chance that the true odds ratio is 5:1 or more. The probability language communicated to me her judgment in a way that the qualitative language failed to do. Similarly in the decision on the swine flu vaccine of 1976 experts in the Center for Disease Control communicated in a qualitative way that there was a serious risk of an epidemic. Decision makers in the Office of the President understood this qualitative language to mean that without a massive vaccination program an epidemic was a virtual certainty. But in interviews after the decision, key experts at the CDC said that their assessment of the probability of an epidemic, without a massive vaccination program, was about 20 percent. It is quite likely that if the decision makers had heard this less ambiguous language a different decision would have been made (more stockpiling and focusing on vulnerable groups and fewer vaccinations actually given).

Second, using probability language for important uncertainties of natural "facts," such as the likelihood that a particular chemical is a carcinogen, helps focus research. For example there are perhaps 400 short term tests for identifying carcinogenic chemicals. It is hard, and inefficient, to sort out the varying predictive capabilities of these tests on a yes-no basis. But if we investigate the tests by using them to make probabilistic predictions for individual chemicals and then score the results, we can begin to see which are the better predictors, and which tests are conditionally linked to others. By analyzing the biological processes of the better and worse predictors and the linked predictors, we may learn things we might have overlooked otherwise. More generally, making predictive probability judgments helps identify the most important uncertainties to resolve and set the research agenda.

Third, quantitative probability assessments are themselves ingredients in decisions. Decisions by policy makers typically weigh values and likelihoods. Often values are quantified by budgets and cost-benefit analysis but judgments of likelihood are left vague and qualitative. As we try to quantify the likelihoods we aid the decision process by making it more systematic and explicit. We help clarify what is more and what is less uncertain and identify the value of existing and missing information.

For example, returning to the example of testing chemicals, the National Toxicology Program needs to choose chemicals to test, to choose particular tests (individual, batteries and tiers) to run, and particular toxic effects to test for. As ingredients to this decision problem, we need some understanding of the predictive values of various tests, the costs of tests, the severity of the effects, and the rarity of the effects. To minimize the expected costs of false positives and false negatives (misclassification costs) some use of judgmental probabilities for unique events is necessary.

How Do We Think About Uncertainty?

The positive question of how we actually think about uncertainty is intertwined with the normative question of how we should think about uncertainty. I will identify what appear to me as a few of the major issues concerning how we actually think about uncertainty, and what seems to me recent changes in perspective.

For the past generation perhaps the most important fact about the way people think about uncertainty has been the split between classical and Bayesian views of probability. Classicists tend to think of probability as objective, in terms of frequencies of repeatable events. Jack Kiefer was a classicist. Bayesians tend to think of probability as subjective, as an expression of individual judgment of uncertainty. To them no events are strictly repeatable, but frequencies of "almost" repeatable events provide a reasoned basis for making judgments of probability. But to them there are additional ways of forming a reasoned basis for probability judgments.

The development I see here is that there is less acrimony between the two camps now than a generation ago. According to Zellner, the Bayesian view is increasingly seen as more helpful in decision making and many of the classical estimators and tests can be shown to be special cases of more general Bayesian estimators. Whatever the reason, it seems that the Bayesian viewpoint seems to be more widely accepted now.

Within the Bayesian camp, we can identify two views about the scope of consistent probability judgment. One view is the ambitious, all-inclusive view. In this view a rational person forms judgments about all possible states of the world and coherent beliefs about the probability of each conceivable state. In its strong form, the all-inclusive view links the belief system of one rational person with another, according to various requirements of consistency and common knowledge.

The second view is less ambitious and more partial. In this view a person will form (fairly) consistent probability judgments within particular models which describe only limited portions of all possible states of world. For example, a person might form probability judgments about what cards his partner might have in a game of bridge, or the probabilities of carcinogenicity in a certain class of chemicals she has intensively studied. Other areas will be left unimpeded and uncharacterized as to likelihood, including beliefs about others' beliefs.

The change I see here is toward the less-inclusive view. Binmore, for example, has argued for this view, as well as for recognizing the dichotomy discussed next.

In forming probability judgments, we can look to the past or to the future. For example, in designing a stormwater catchment basin, we may look to the past history of flooding to estimate the size and pattern of a thirty year flood and a hundred year flood. These backward-looking analyses help us assess probabilities of floods of particular sizes next year, and over longer periods of time. Alternatively, we sometimes form probability judgments by constructing models, considering initiating events, and projecting forward (probabilistically) causal chains. This is done in analyses of nuclear safety.

Of course, in practical situations, people use both forward- and backward-looking methods to form judgments about uncertainty. I do not see much change in the past several years toward one or the other perspective, but perhaps there is now a greater appreciation that there are two perspectives here. I think that this awareness is useful because the two perspectives involve different styles of thinking.

I associate the forward-looking perspective with much of what we call rational analysis. To a large extent it is what game theorists do when they analyze the Bayes-Nash equilibrium of a game of incomplete information. In contrast, I associate the backward-looking perspective with evolutionary processes. For example, funnel spiders living in the desert will compete for locations for their webs. A spider without a good location will approach a web in a good location, shake the web, and depending on the response, decide whether to fight the "owner" for the spot. This process can be modelled as a game of incomplete information, also with a Bayes-Nash equilibrium (fairly predictively it appears), but we do not think of the spiders as game theorists rationally looking ahead at the consequences of alternative actions and making expected utility calculations. Instead we think of various strategies "hard-wired" into their genes, with the fittest strategies, proliferating over generational time.

In a rough parallel, I think the heuristics that cognitive psychologists have found people to use in constructing judgments of uncertainty to have a rather strong emphasis on backward looking. Certain strategies that have worked pretty well in the past, such as the *availability* heuristic (recalling frequencies of similar events) are applied to a present case. Fischoff and others have found that experts as well as lay people use such heuristics. But it seems that experts tend to rely more on more "rational" forward-looking methods (analyzing symmetries, doing fault tree analyses). Since these two styles of thinking are different, mixing the two together may lead to miscommunication. For example, in *Risk and Culture*, Douglas and Wildasky analyze risk assessment, as done by experts. But the authors make their analysis largely in terms of the (anthropological) concept of danger, which is largely backward looking. By not explicitly recognizing the differences in the two styles of thinking some misunderstanding may have arisen in the book.

Current and Future Research

How one comes out on these three issues -- Bayesian vs. classicist, all-inclusive vs. partial, and forward vs. backward looking -- provides alternative perspectives or vantage points in thinking about uncertainty. Our current research is exploring a vantage point which emphasizes the Bayesian, partial, and backward-looking perspectives (without exclusive focus on this mix). For example we are investigating the combination of forward- and backward-looking perspectives. (And since the interaction of the two perspectives is particularly interesting to us I have put them in the title of this note.)

From these vantage points -- weighted toward the Bayesian, partial, and backward looking -- we are investigating how people, acting under competing incentive structures, make decisions with incomplete information. In making their decisions, individuals take actions which may benefit themselves, but the actions may reveal part of their private information. Thus people may develop *action* strategies which directly benefit them and *information* strategies which may indirectly benefit them by keeping information from others or acquiring it from others.

We have found that in both our theoretical and experimental work that action and information strategies interact in complicated ways, even for simple games. Under certain conditions a sequential game will lead to consensus about the decision relevant information. We have been able to identify sufficient conditions for this consensus, for a fairly general structure of game, as long as people have "truthful" dominant strategies.

But there are many open questions remaining. We still do not understand very well how action and information strategies interact. We know that sometimes the consensus is fully revealing in information, sometimes not, but so far we do not have a useful characterization for when the consensus will be fully revealing. We do not yet have general characterizations for the number of steps it takes for a particular process to converge.

In our experiments we have explored how closely people come to the theoretically predicted results of consensus and full revelation of information. Preliminary results suggest that people come part way toward the theoretical predictions, but they are not fully rational in the forward-looking sense.

Among other things this finding has encouraged us to rethink the notion of a Bayes-Nash equilibrium. We are attempting to place it in a backward-looking context as well as its more traditional forward-looking context. This leads us to ask somewhat different questions of simulation. In particular, if various autonoma having different strategies "wired-in" played against one another, somewhat like the funnel spiders, and the more successful proliferated, would there be long term stable and predictable outcomes? This question leads us to think more about the dynamics of the process toward equilibrium, and to think about the long-standing problems of multiple equilibria from a different perspective. In particular some of the recent work on chaos may be useful here.

Application

I will conclude with a few words about how this research may contribute to a more rational environmental policy and provide a communication bridge between "producer" and "consumer" communities.

This time I will start with the more controversial and work back to the more settled. To some, a "rational" environmental policy is a policy where one attempts to maximize expected value (or utility). In calculating and comparing expected values, quantitative assessments or probability are required (especially including assessments for unique events). In this view any research which helps us understand how we make probability judgments, and helps improve our skills in making them, is likely to contribute to a more rational environmental policy.

However, expected utility has recently become a more "iffy" concept, both normatively and positively. Some will find it a too narrow (and now shaky) grounding upon which to include other values, such as equity, or process considerations, and so on. But even with this broader view, it is still important to understand how we assess uncertainty and how we can improve our skills. Supposing we, as a society, want to be fair in spreading the risk costs from ozone depletion and AIDS from blood transfusions. We still want to know how likely these effects are, under what circumstances and with what mitigation opportunities.

So far the uncertainties we have studied have come primarily from two sources. One source is "easy," arising from statistical information and random processes. For this type of uncertainty conditional probabilities can be calculated canonically and performance studied unambiguously. The second source is "hard," having to do with anticipating and analyzing others' decisions (and involving more ambiguous notions of equilibrium). Both types of uncertainty have application to environmental decision making, particularly the second, when decisions are made in groups.

But there is a third source, which comes from the uncertainties of the environmental problems themselves. These uncertainties are less stylized and tractable and thus less easy to analyze. However, in principle, it is possible to study them as long as the following condition is met: after the initial decisions are made there is improved information upon which to evaluate them (and the wait to the improved information is not too long). This condition is met for evaluating weather forecasters, where in fact a great deal of probabilistic decision making is made and evaluated; it is met for chemical testing and for many experiments. But so far we have concentrated on more stylized theoretical and experimental controlled aspects.

As to a bridge between producer and consumer communities, consider the vantage points identified above. It seems to me that the producer community is predominantly comprised of experts who tend to be classicist, all-inclusive, and forward looking. (Many have little statistical training, being scientists in specific areas, but those who have some statistical and probability background tend to be classicist.) They also tend to be deductive and formal. In contrast, the consumers tend to be more Bayesian, partial, and backward looking. They tend to rely more on heuristics and to form beliefs on direct past experience. Insofar as they talk about probabilities at all, they have no trouble talking about the probability of a unique event.

At least this was my experience while a guest scholar in the Office of Pesticides and Toxic Substances in EPA. The GS 14s and 15s (the producer experts) talked like classicists, while the assistant administrators held many of the attitudes of Bayesians (but without the language or formalism). And they often talked past each other. There is the same sort of gap between scientists and engineers on one side and policy people, decision makers, and the public on the other.

To the extent we become more aware and understanding of the characteristics and causes of this gap, we will be better able to communicate across it.

Discussion: Decision Making in the Environment

Mitchell J. Small
Department of Civil Engineering
and Engineering and Public Policy
Carnegie Mellon University
Pittsburgh, Pennsylvania 15213

Page raises a number of issues on the nature of uncertainty and how decisions are made in response to uncertain environmental risks. Many valuable insights result from recognizing the different modes of uncertainty analysis and perception, and Page's framework should allow continued advances in this understanding. I wish in this discussion to take a small step back from these issues to address the broader question of why environmental engineers and scientists involved in studying the fate of environmental constitutents must, and will, become increasingly aware of the issues of uncertainty and risk perception, traditionally the realm of the social sciences.

Consider the major components of the environmental system: pollutants are discharged to the environment, the pollutants move through the environment undergoing various physical, chemical and biological transformations, and impacts occur as target organisms are affected and the beneficial uses of resources are curtailed. Human decision making impacts this system in two major ways. First, decisions are made on the initial releases, determining which chemicals will be banned, controlled or emitted to the environment in differing amounts. This is the classical type of environmental decision; made by those in control, either in industry or government. The second type of decision making occurs *within* the environment, as people decide which products to use, which activities to engage in, and which environmental risks they will respond to, through both personal choice and collective action. Each of these types of decisions is made with differing levels of information and different modes of response to this information. Understanding how the perception of uncertainty and risk affects decision making is thus critical to understanding how pollutants are introduced to the environment, as well as how they flow within and through the environment.

Page provides a number of examples of the first type of decision maker: officials in the Office of the President determining the need for a flu vaccination program and the assistant administrators at EPA determining the final form and content of a regulatory program. The insights from Page's research for these types of decisions are very important. While the environmental engineer (the producer of environmental research) tends to have a formal and analytical (forward-looking) view of uncertainty, the decision maker tends to maintain a less formal, experiential perspective. How to bridge this gap? One possible approach is to consider the difference between the traditional tools environmental engineers have used to aid decision makers in formulating policies, such as optimization methods, in contrast to the newly emerging tool of expert systems (e.g., Jennings, 1987; Ortolano and Steinemann, 1987). The former tend to be based on well defined and rigorous mathematical statements of utility, constraints and probability (the engineering science approach), while the latter tend to be based on less formal, heuristic rules (the decision makers approach). Research is clearly needed to bridge the gap between these methodological approaches. This research may also help to bridge the gap between the engineering and decision making view of risk and uncertainty.

The second type of decision making that occurs in the environment is that by people potentially exposed to the risk. In many emerging environmental problems, the disaggregate decisions of individuals largely determine the level of population exposure. Consider two examples:

- indoor radon -- homeowners must decide whether to sample radon concentrations in their homes, and, if the result is above some action level, decide whether to undertake mitigative action. (Svenson and Fischoff, 1985; Small and Peters, 1988).
- lead in drinking water -- homeowners must decide whether to test their water and subsequently modify their water supply.

In these examples, the psychology of risk perception, risk communication and decision making play a critical role in determining the ultimate population exposure, along with the physical chemistry of radon migration in soils and homes and lead corrosion in water distribution systems. The engineering and social aspects of the problems must be considered together if accurate exposure assessments are to be performed, and effective exposure-reduction strategies developed.

Some additional examples:

- water conservation -- public beliefs and awareness greatly impact the level of water use during droughts (Bruvold and Smith, 1988).
- sea-level rise -- decisions to rebuild or retreat from coastal areas following storms will determine the impact of rising oceans.
- hazardous waste facility design and siting -- public perception of risks continue to limit which types of facilities are built and where.

The processes which affect human behavior and disaggregate decision making clearly help to determine the level of environmental impact. Of particular importance to the management of hazardous wastes is the tendency for a social amplification of risks (Kasperson et al., 1988), whereby risks which experts deem to be small become amplified in the public eye until a seemingly beneficial project becomes impossible to implement. The development of an effective hazardous waste management program must consider these social processes in conjunction with the engineering and scientific processes which determine pollutant fate, such as incinerator destruction efficiency and biochemical degradation in soils. In the future, simulation models for environmental problems will link these components of pollutant transport with models of human decision making to provide a comprehensive representation of environmental systems.

Human decision making plays a critical role throughout environmental systems. The recognition of the need to incorporate this role in environmental assessments has brought us to the edge of an exciting new era of cooperative research between decision scientists and environmental engineers, and will ultimately lead to a better understanding of the environment and an improved ability to manage its problems.

References

Bruvold, W.H. and Smith, B.R. (1988) Developing and assessing a model of residential water conservation, *Water Resources Bulletin*, 24:661-669.

Jennings, A.A. (1987) Algorithms for automated regulatory review of hazardous waste management facilities, *Environmental Software*, 2:138-145.

Kasperson, R.E., O. Renn, P. Slovic, H.S. Brown, J. Emel, R. Gable, J. Kasperson and S. Ratick (1988) The social amplification of risk: A conceptual framework, *Risk Analysis*, 8:177-187.

Ortolano, L. and A.C. Steinemann (1987) New expert systems in Environmental Engineering, *J. of Computing in Civil Engineering, ASCE*, 1:298-302.

Small, M.J. and C.A. Peters (1988) Public Policy model for the indoor radon problem, *Mathematical Computer Modeling*, 10:349-358.

Svenson, O. and B. Fischhoff (1985) Levels of environmental decisions, *J. Environmental Psychology*, 5:55-67.

Summary Discussion - Multiphase Systems

Perry L. McCarty
Department of Civil Engineering
Stanford University
Stanford California 94305

This session on systems dealt with a range of complex environmental issues including the concentrations of chemicals that might cause environmental harm; properties of chemicals and phases that permit one to estimate movement, reactivity, and effects; importance of boundaries between phases in concentrating contaminants and impeding or enhancing their transfer rates between phases; and how to convey properly to decision makers the scientific understanding available and the relative importance of the environmental issues before us. Because of the complexity of the problems and the great many unknowns, it is not easy to formulate the questions of most importance for future research. On the other hand, the presentations and discussions revealed that much progress in understanding has been made since the last AEEP conference on environmental engineering that was held about six years ago.

The need for more information on factors affecting reactions and their rates was repeatedly indicated. While the significance of biological processes in transforming chemicals and the need for more information in this area was expressed, the importance of chemical processes, and especially the importance of photochemical reactions was also indicated. Several comments were made on the possible significance of biota other than microorganisms in concentrating and transforming contaminants, as well as their potential use for evaluating the past history of some contaminants and their role as vectors in human exposure. The part that may be played by trees, grasses, and other vegetation in the movement and fate of contaminants was felt to be in need of study because they are significant features of the landscape and are of environmental importance in their own right.

An issue that continued to surface as of major importance was the lack of sufficient environmental data on the movement, transformation, and fate of contaminants. In this vain a dominant theme of the presentations and discussions during this session was on the use and value of models. Associated with this was the obvious lack of good environmental data with which to calibrate models. It was recognized that models are often used for estimating environmental exposure, and such data are badly needed for model calibration. Many agreed, however, that research funds are inadequate for obtaining the environmental data needed. Both laboratory studies, which are less expensive than field studies, and modeling, which is perhaps less expensive than either, were thought to be preferred by funding agencies because of lower cost. However, there was the belief expressed that the use of models developed without the availability and use of field data for proper verification is dangerous and likely to lead to improper conclusions by decision makers.

The participants tended to agree that models serve many purposes, and at times, a relatively simple model can provide hypotheses to help guide research, while more comprehensive models can help bring together an understanding of physical, chemical, and biological processes within and between phases that cannot be done in any other way. Overall, it appeared to be the consensus that both modeling and experimental work need to be done, and that those working in each area should do so with sensitivity to the need of the other and with recognition of the importance of both efforts. In application of models one must be sure that the model being used is appropriate for the question being asked. Also, the use of models was indicated to be worthwhile, even in cases where there is great uncertainty, but with the caveat that the degree of uncertainty needs to be explicitly stated. This led to subsequent discussions about the need for more studies on how to address the great problems of uncertainty in our understanding of the environment, and in models developed to codify that understanding. How to adequately address uncertainty is an issue of great importance in development of models that are to be used for evaluating contaminant movement and fate, and for decision making. These discussions further emphasized the great need for close interchange between scientists, engineers, and, as well, with social scientists who are concerned with decision making and questions of uncertainty.

Summary Remarks

James J. Morgan
Marvin L. Goldberger Professor of Environmental Engineering Science
California Institute of Technology
Pasadena, California 91125

On special occasions such as this, I like to recall what Mark Twain is said to have remarked on the occasion on his hanging: "If it weren't for the honor of it, I'd just as soon pass!" I might describe my "conference career" as a scientist and engineer in this way: Early in my career, I gave only research talks. As time has progressed, moving toward "infinity", I find myself increasingly called upon to be a co-chair or a rapporteur. In an imaginary "phase diagram" of the career, the early data points would fall in the research domain; as I assume more and more the role of co-chair and rapporteur, my coordinates have eased toward 100% absorption with "CC" and "Rap" in the neighborhood of infinity. Remarkably, in this corner of phase space, it occasionally comes to pass that other folk present some of my laboratory data as part of their research talks, a far greater honor than the one Mark Twain remarked on.

The Universal Environmental Diagram

Before moving to some of the philosophical remarks that Dick Luthy invited me to undertake, let me ask you all to picture with me a universal environmental diagram. When I was a graduate student at Harvard, it was a goal of a few of my laboratory colleagues and myself to create that one slide, a perfect, multiple purpose visual aid, which could be used on the occasion of every talk and which would be completely information-free and value-free. Such a device could, then, in the playful spirit of our luncheon speaker yesterday, be adapted to every occasion, so that only the answers need be changed! The diagram I would like you to imagine now has a horizontal line, with eleven (full) circles above the line and eleven (empty) circles below the line. Now, depending upon your inclinations and sense of recall for events of yesterday and today, the diagram represents either the trees around Atlanta (constituting a potential source of ozone, thus fulfilling the early insight of Governor Reagan); or, they are the atmosphere/water interface, with gas molecules and aerosols making ingress and egress; or, they are a particle/water interface, with O'Meliaesque polymers and ions struggling for position; or, the craftier among you will recall it as a losing formation from last night's Monday Night Football game!

Who's in Charge Here?

But there is a more serious aspect to sports metaphors, and it has something to do with play calling. At this conference we seem, from time to time, to have worried about what we're not. I recall at least a half-dozen occasions on which a speaker or discusser said: "But I must point out that I am not an environmental engineer." At one point this morning, a speaker said, "I'm not an engineer, I'm just a simple chemist." (Now, when was the last time you met a simple chemist?) An engineer yesterday felt it necessary to remind us that he was not a microbiologist. In the football metaphor, an issue seems, at times, to be: 'Who gets to play quarterback?' I will argue, later, that this should not be an issue, but that it does seem to tie us up, or slow us down, when we are trying to understand one another's points of view. In my own experience, which goes back some thirty-five years, the question 'who is the quarterback?' has evolved over time. I started out a simple civil engineer, and then became an extremely more complicated water chemist. Rather than changing identities, I believe I accumulated them. Perhaps this has given me a little insight into how interdisciplinary or multidisciplinary environmental work gets accomplished. I hope so. One thing I learned early in my career: the role of 'handmaiden' should be rejected by any self-respecting scientist or engineer in the university.

A Perspective on Scales

Imagine with me one last "figure" before I move to the podium to preach (if you hadn't noticed that I wasn't preaching yet). Our imaginary figure is a framework for considering time scales and length scales. A theme that I have noticed throughout our conference is the very wide ranges in scales which we must grasp and deal with in environmental science and engineering. Our time scales of interest range from about 10 femtoseconds to about 10 billion seconds, a wide range indeed. Our length scales range from about a tenth of a nanometer to perhaps 40 thousand kilometers. I leave it to each of us to find our own scales of interest on such a diagram. In our conference we have discussed the scales of urban smog, filtration, coagulation, the chemical dynamics of the upper atmosphere, movement of pollutants through ground waters, the microbial world, and many other areas of shared interest. Time scales and length scales are things that set us apart from one another in the literature, but not fundamentally, I think. On the first day of this conference it was said, correctly I believe, that many of us must in our work span very, very wide ranges of length and time scales. To which we can say: so be it. Many scientists and engineers need to do that these days; environmental scientists and engineers must do it to an unusual degree, as manifested by our discussions at this conference.

In 1977 and 1982 there were two predecessors of this conference, both of which I was fortunate enough to attend. The range of subjects and environmental scales considered at those two conferences was much narrower. Today, our conference has addressed chemistry of gases and particles in the atmosphere, the breakdown of organic contaminants in groundwaters, persistence of viruses and bacteria, and recent developments in risk analysis. We deal with time scales as short as those of electronic motion and transport-controlled chemical reactions and as long as those for ocean mixing and the storage of hazardous materials of very long lives. To be an engineer in our day is not to deal solely with mass transfer and energy transfer in large-scale systems. To be an engineer is to design systems that work at the length and time scales of modern electronic devices; or, to design large structures that will withstand severe earthquakes; or, to design control strategies for water or air pollution systems on local, regional, or national bases. I think that, to our disadvantage, we can define our field of environmental engineering too narrowly, because the "playing field" has changed in many ways. The newer "game" does not mean that civil engineering and chemical engineering are not relevant: They are. What I believe it means is that all of science and much of the rest of engineering is now potentially relevant.

The environmental field cannot complete for society's attention on a national agenda by arguing for traditional ways of looking at complex, new problems. We must challenge our profession to examine the ways in which engineering is changing. I agree in spirit, if not in detail, with the remarks made by the Director of Engineering for NSF yesterday. We may have become too specialized, too divided. We may well have too many varieties of departments at our universities. Perhaps there are too many kind of divisions in the National Science Foundation. We need to be concerned about the proper place of environmental research in all of this, of course. But, the organizational questions aren't the sorts of questions that state legislatures or the Congress want answered, at least in my own experience. They don't want to know the exquisite nature of your discipline. They want to know what we are going to do to help them for judgments about how to solve water pollution problems, air pollution problems, and problem which may be both, or neither.

It was a sobering experience to appear before a committee of the California legislature in 1981, to testify on behalf of legislation which would support acid deposition research in the state. For an hour or more I was asked to justify the need for research on the subject in terms of the answer to but one question: "do we or do we not need to further control emissions of nitrogen oxides?" Only when those of us testifying were able to explain convincingly to our interrogators that we did not really know enough at that point to answer that one question decisively was the need for research made clear; and a $20 million research and monitoring program was created, one which has helped to establish the basis for future regulation of emissions in the state, and which has helped to reveal the characteristics of acid depsition in the western states. It is important, I believe, for all of us to have a deep grasp of our individual disciplines yet be able to relate to the larger issues which span the time scales and length scales of our environmental profession.

Short-term Problems vs. Long-term Questions

To find answers to complex questions and solve complex problems, we will probably have to take a longer view, get beyond the immediate narrow questions or problems that can be easily seen. Consider the guillotine! During the Reign of Terror in the Revolution, a chemist, a biologist and an engineer, all convicted of crimes against the Revolution, were to face the guillotine. The chemist went first, was offered the usual choice: face up or face down? He bravely chose face up, the cord was yanked, but the guillotine blade did not fall. The chemist was spared. The biologist followed, made the same courageous choice, and was also spared, when the blade, once again failed to fall. Then it was the engineer's turn. He too chose bravely, looking upward at the instrument of his execution. As the cord was to be pulled once again, he shouted out: "Wait a minute, I think I see the problem!" A limited vision may prove fatal. Change the order of execution, change the professions; the lesson is the same. We should watch out for the narrow view!

Integration

Dick Luthy, our Conference Chairman, asked me to say something about why we came together here, what we hoped to accomplish, and what we ought to be doing next. I will not rehearse the conference for us. We have all listened, we all have made out notes and jottings.

It is a little unusual for me to remain silent through such a stimulating conference for so long. I thought my reward would come, in time. I think this has been a marvelous conference in many ways, both because of the rich details of the science, the engineering, and the social science information that we have received, but also because of the general ideas that have been put forth. A dominant theme of the conference strikes me as integration, in several ways. We have heard of integration of information from theory, laboratory, field and models. I make a distinction, revealing my prejudices, between theory and models; not all of our models are grounded in theory. As our science and engineering of the environment develop, more of our models should have a firmer basis in theory. Integration, from theory to application, predicting the behavior of environmental systems, whether they be land, water, air, or all of these is one of the major themes of our conference. I believe that such integration cannot be achieved in the perspective of science alone, nor can it be achieved by working solely in the context of specific applications. Scientists, engineers, and risk analysts must ask relevant questions of one another: what are your concerned about? what are your important questions? your new data and models?

Dialogue

The integration we need results from sustained dialogue among members of the concerned community, in this context our community of environmental scientists and engineers. We heard a provocative slogan yesterday: "First pick up the journal, then pick up the phone!" Or, if you're in your lab, get out and walk down the hall to your colleague's lab. The literature alone will probably not sustain us. Too much of it! We need to engage one another in dialogue about the things that matter most to our profession. We need to debate those technical questions, problems and issues that are keys for us. I recall a 1984 Gordon Research Conference session on the sorption of organics and the effect of solids concentration on pollutant partitioning. Dominic Di Toro of Manhattan College and Phil Gschwend of MIT had just engaged in an intense debate about the data and theory. And I recall Phil saying, as time ran over, "It's a blast arguing about science with you!" I remember thinking, that's at the heart of it, because these colleagues really cared about their subject and they went at it intensely. They were engaged, and the other participants were, too, as a result.

Hierarchies and Frequencies

Interdisciplinary work is hard work. When it goes well it can be great fun. Often it is frustrating. The stretch of disciplines can be demanding. Of course, if we don't stretch, we can avoid the frustrations, and the benefits as well. I think this meeting is an excellent model for both the frustrations and the benefits of spanning many disciplines. From my personal perspective, having been at the 1977, 1982 and now the 1988 conference, 5 to 6 year intervals are too long for what we need in our profession. Too much changes over 5 to 10 years. Scientific advances, for example in molecular biology, biotechnology, chemistry, and risk analysis need to be absorbed and integrated more rapidly. This conference now has opened up to air quality issues, and has much greater representation in multi-media research than its predecessor conferences. I realize that a consequence of devoting so much time to new issues is that less time is available for some important problems, still not completely solved, that featured prominently at earlier conferences. Some of the hard issues from 1977 and 1982 are still with us, and now we have newer ones! We are concerned about urban photochemical smog, about global atmospheric changes, about regional acidification, about more sophisticated risk assessment, and so on. In speaking to people individually at this conference, I sense the frustration that can attend greater complexity. What is the answer? I think it is: Hold conferences of this kind more frequently in order to promote an exchange of ideas along the lines we have experienced here. Let us learn how to avoid (or if not, enjoy) those "tangled hierarchies" of which Paul Roberts spoke. I doubt that it matters who "goes first" in multidisciplinary research, but it matters very much that we know what the truly important questions and problems are. We need to meet more often, discuss our goals, and come to some consensus about the important problems.

Fragmentation

Science and engineering on large-scale environmental systems may face some new difficulties ahead with respect to integration of work along the lines mentioned above. There is a hazard for university researchers in a kind of science or engineering that gets funded by agencies contracting for field data, laboratory data, and other components of the environmental information matrix, if the agencies in turn carry out their own comprehensive interpretation and modeling on the path to policy formulation. There is a danger to the integrity of research in the universities from this way of organizing environmental research. It is difficulty to see students through a substantial doctoral project on this basis. I believe that this community of researchers ought to reflect seriously on this matter of environmental research management. The style of funding I describe has already had some impact in the atmospheric area: fragmentation. There is, evidently, a strong incentive for some government agencies to say "We know what it needed. We'd like the nitrogen data from so and so, the sulfur data from someone else, the meteorology from another group, and so on." The consequences can be detrimental for university research, unless provision is made for access to essential data on the part of research groups. Integration of joint research really calls for planning by all concerned: scientists, modelers, engineers, analysts, and others. All should be participating in design of large-scale research at the outset. The management of large environmental data bases is become an increasingly important aspect of environmental research and policy formulation. If integration is one of our themes, then we must pay increasing attention to data access for the concerned community of environmental scientists, engineers and policy makers.

A Shared Vision

I would like to conclude by returning to the vision of the conference and of AEEP that Dick Luthy shared with this group at the outset. What I hope that we might all "take home" from our time together here is a shared vision of what is required of us to have excellence in environmental engineering education and research. What is demanded of us? What lies beyond high sounding phrases? I believe this conference provides an answer. I'd like to underline it. What is demanded of us is recognition of the complexity of many of the environmental systems we deal with; the complexity of water systems in themselves, of air systems in themselves, and the still-greater complexity of water, air and land systems together. I think we need to recognize that we must base environmental actions: regulations, design and enforcement, on the best fundamental information that we can command. And by 'fundamental information' I don't mean only scientific information. I mean the whole set of information that involves physics, chemistry, biology, ecology, engineering, economics, risk analysis, policy analysis and other fields. I see it not as a hierarchical structure, but a structure of relevance to environmental concerns, things that are essential to translate knowledge into solutions. We need the best information; we will not always have that. Engineers will understand what that often means. When you don't have ideal information and you face a decision, you design the best sytem possible, and you explain to the client what the limitations are, what the uncertainies are. Whether these risks are acceptable is a matter for further discussion of policy.

Vision and Relevance

Environmental work of the highest order demands both science and engineering. I see no dichotomy between science and engineering in the modern era. Some of the strongest academic programs in the U.S. and in Europe are based on departments populated with both scientists and engineers, often many kinds of scientists and engineers. The key, I think, is constantly looking out for the relevance of our disciplines to the problems the environment presents, seeing where the disciplines merge, where the interdisciplinary possibilities are. As more than one speaker has said at this conference, our work now demands a multi-media awareness in the investigation, design and management of environmental systems. Our collective vision cannot be limited to laboratory research alone, to models alone, to field work alone. Integration and vision imply that we pay attention to all of these aspects. We advance by specialization. That is the nature of the modern Ph.D. But, if we specialize in the environmental profession to the exclusion of awareness of that which is truly relevant to our community of scientists and engineers, then we accept limitations which may defeat us, ultimately. While we advance through specialization, it is not enough for problems of the complexity that we increasingly face.

Specialists and Everything

Wittgenstein said, "Die Welt is alles, was der Fall ist." The world is everything that is the case. So it is for the environment. To paraphrase another remark of Wittgenstein, as specialists, we feel ourselves absolved from whole realms of existence. There is some truth in that, and implications for environmental work, obviously. We can escape into our specialties, achieve success through them. We may form schools, with branches, on the nature of ion adsorption onto an oxide surface (I promised Dick Luthy that I wouldn't mention that!), or pursue a true understanding of the hydrophobic effect at a graphite surface. These are important and valuable, in perspective. But these are not goals, they are means to a fuller understanding of environmental systems.

Concern for the Environment Unites Us

What unites us is more important than what separates us. Environmental engineers and scientists are united in a concern for and sense of responsibility for the environment. Our strength must be solidly founded on understanding fundamentals and appreciating the relevance of the sciences and engineering to environmental systems and environmental decision-making. We all have our own person reasons for the work we have chosen. It will be "a blast" for us, I hope. And what do we should matter for the environment. That is what unites AEEP, I believe, because what we do matters for the water environment, the air environment, or the whole environment.

Seeing What is Urgent

I've learned about many important problems and issues at our conference. I value this occasion for what we have discussed and debated. One thing I believe is left over. That is a sense of what the urgent problems are at this time. If we can place our concerns with some accuracy along the line from interesting to important to urgent, that might be a valuable contribution to national dialogue on environmental priorities. One and a half days is a short time in which to reach such a goal, and when we say "urgent" research problems, we need to know what we mean it. Consider the question: What truly commands our highest sense of priority as environmental researchers? Should it come to pass (in fantasy) that you and I appear together on *The McLaughlin Group* or *Firing Line* or (perish the thought), *Geraldo,* with "air heads" on one side and "water heads" on the other, let's hope to have our priorities together. Real-world situations call for a sense of what is urgent, what the agenda bottom line is. When we sit down to make council with the policy makers, the legislators, the agency people and others "out there", I doubt that they will really care about what we find fascinating. They will really care about the agenda for society and what we believe is essential for environmental protection and improvement. Until we meet again -- and it will be sooner, I hope -- let us ponder what is urgent for the environment, as well as what each of us would like to do now and in the longer run.

APPENDIX

Conference Program

Fundamental Research Directions In Environmental Engineering
Key Bridge Marriott Hotel, Arlington, VA

Sunday November 13

Evening Reception; 7:00 P.M., Potomac Room - Welcoming Remarks and Objectives of the Conference, Richard G. Luthy (Carnegie Mellon)

Monday, November 14, Potomac Room, 8:30 A.M.

Physical Processes, Chairman, John H. Seinfeld (Caltech)

	Air	**Land**	**Water**
Speaker	8:40 Ken Demerjian (SUNY Albany)	9:20 John Wilson (NM Inst. Min. & Tech.)	10:00 Paul Roberts and Jeffrey Koseff (Stanford)
Discussant	8:55 Phillip Roth (Consultant)	9:35 Linda Abriola (Michigan)	10:15 Desmond Lawler (Texas)
Floor Discussion	9:00-9:20	9:40-10:00	10:20-10:40

Chemical Processes, Chairman, Philip C. Singer (UNC), 10:45

	Air	**Land**	**Water**
Speaker	10:45 Michael Hoffmann (Caltech)	11:25 Bill Glaze (UCLA)	1:30 Charlie O'Melia (John Hopkins)
Discussant	11:00 Harvey Jefferies (UNC)	11:40 Rene Schwarzenbach (EWAG)	1:45 Steve Eisenreich (Minnesota)
Floor Discussion	11:05-11:25	11:45-12:00	1:50-2:00

Lunch: Noon-1:15, View Restaurant

Speaker: John A. White, Jr. Assistant Director for Engineering, NSF
"Engineering in a Changing World"

Biological Processes, Chairman, C.P. Leslie Grady Jr. (Clemson) 2:15

	Risk/Toxicology	**Land**	**Water**
Speaker	2:25 Michael Gough (Resources for the Future)	3:05 Alexander Zehnder (Wageningen)	3:45 Sandra Woods (Oregon St.)
Discussant	2:40 Joe Rodericks (Environ)	3:20 Jim Tiedje (MSU)	4:00 Bruce Rittmann (Illinois)
Floor Discussion	2:45-3:05	3:25-3:45	4:05-4:25

Evening Banquet, 7:30 PM, Potomac Room

Speaker: John A. Moore, Acting Deputy Administrator EPA
"Research Strategies for the Environmental Protection Agency"

Tuesday, November 15, 1988

Multiphase Systems, Chairman, Perry L. McCarty (Stanford) 8:30

	Air	**Land**	**Water**	**Systems**
Speaker	8:40 Yoram Cohen (UCLA)	9:20 Don Mackay (Toronto)	10:00 Jerry Schnoor (Iowa)	10:40 Talbot Page (Brown)
Discussant	8:55 Ron Hites (Indiana)	9:35 Phil Gschwend (MIT)	10:15 Christine Shoemaker (Cornell)	10:55 Mitch Small (CMU)
Floor Discussion	9:00-9:20	9:40-10:00	10:20-10:40	11:00-11:20

Conference Summary, Rapporteur, James J. Morgan (Caltech), 11:30-12:30