Pacific Northwest Laboratory

**FY 1995 Research Highlights:
PNL Accomplishments in
OER Programs**

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Pacific Northwest Laboratory
Richland, Washington 99352

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R.I. Samoilova, Institute of Chemical Kinetics and Combustion, Russian Academy of Science

Introduction

Pacific Northwest Laboratory (PNL) conducts fundamental and applied research in support of the U.S. Department of Energy's (DOE) core missions in science and technology, environmental quality, energy resources, and national security. Much of this research is funded by the program offices of DOE's Office of Energy Research (DOE-ER), primarily the Office of Basic Energy Sciences (BES) and the Office of Health and Environmental Research (OHER), and by PNL's Laboratory Directed Research and Development (LDRD) Program. This document is a collection of "research highlights" that describe PNL's accomplishments in DOE-ER funded programs during Fiscal Year 1995. Included are accomplishments in research funded by OHER's Analytical Technologies, Environmental Research, Health Effects, General Life Sciences, and Carbon Dioxide Research programs; BES's Materials Science, Chemical Sciences, Engineering and Geoscience, and Applied Mathematical Sciences programs; and PNL's LDRD Program.

BES-funded research at PNL is key to the Laboratory's commitment to establish a world class science base in chemistry, materials, geological, and computational sciences. Programs supported by BES provide strong contributions to DOE missions in basic science. PNL's BES-funded research programs focus on achieving an understanding of the complex, multidimensional environmental problems associated with the production and consumption of energy and the cleanup of contaminated sites that resulted from the past use of inadequate environmental protection practices by the federal government and industry.

PNL's research for OHER increasingly focuses on problems that require multidisciplinary scientific teams to address the multitude of time and spatial scales found in health and environmental research. Our health effects research for OHER ranges from the study of fundamental physical and chemical processes to the mechanisms by which hazardous physical and chemical agents affect living systems. Our environmental research ranges from studies of the effects of natural events and human activities on the environment to development of technologies to minimize environmental impacts and remediate damage caused by human activities. PNL is also developing the Environmental Molecular Sciences Laboratory (EMSL) with sponsorship from OHER. The EMSL will be a major research center for collaborative research related to the environment.

PNL's LDRD Program supports new and innovative projects throughout the Laboratory; however, the Laboratory's core competencies are targeted for emphasis. These competencies are 1) integrated environmental research, 2) process science and engineering, and 3) energy systems development. While emphasis is placed on these core competencies, LDRD funding also is allocated for projects judged to have high scientific/technical merit that are independently proposed by individual researchers or multidisciplinary teams working in collaboration. PNL will continue to focus the majority of its LDRD investments in the development of scientific and technical areas that underlie PNL's three core competencies. Examples of such areas include the environmental sciences, biological sciences, computer and information sciences, chemical and materials processing, and energy technology.

Research funded by DOE-ER is the basis for PNL's contribution to the nation's science and technology leadership, and the fundamental knowledge resulting from PNL research contributes to DOE's missions of environmental quality, energy resources, and national security. Our research is beneficial to DOE in determining its direction regarding scientific research, technology development, risk management (technical, social, economic), and science and technology policy.

KC-02 Materials Sciences

Biologically Inspired Coatings

Principal Investigators: A.A. Campbell, G.L. Graff, P.C. Rieke, S. Baskaran, B.C. Bunker, and J. Liu
Funding Source: Office of Basic Energy Sciences, Division of Materials Sciences (KC-02)

"Biomimetic" research at the Pacific Northwest Laboratory has resulted in the development of a low-temperature aqueous solution method for the formation of ceramic coatings on a wide variety of materials. Coatings have been made that have magnetic, bioactive, and/or protective properties. Unique advantages of this process over plasma-sprayed coatings include uniform coating on a wide variety of shapes and materials, including porous surfaces; aqueous environment at temperatures less than 70°C; and ability to control the phase of the deposited material. This biomimetic coating process is being used to deposit bioactive minerals on orthopedic implant devices, which has proven far superior to any other coating process since it minimizes implant rejection and maximizes the healing rate.

Dense, uniform mineral coatings have been grown onto a wide variety of substrates using the biomimetic process developed at PNL. Development of this process was inspired by the observation that, in nature, living organisms use various macromolecules to control the nucleation and growth of mineral phases. The biomimetic process mimics nature's process of template-mediated mineralization by chemically modifying substrates to produce a surface which induces heterogeneous nucleation from aqueous solutions. Rather than using complex proteins or biopolymers, the biomimetic process employs surface modification schemes which place simple ionic functional groups on the underlying substrate. Once the substrate has been chemically modified, it is then placed into an aqueous solution containing soluble precursors of the

desired mineral coating material. Solution pH, ionic concentration, and temperature are maintained in a regime where the solution is supersaturated with respect to the desired mineral phase, thereby creating the driving force for nucleation and growth.

In addition to being less expensive and less complex than current coating methods, biomimetic coatings provide 1) the ability to control the thickness and density of the deposited mineral phase; 2) an easy way to coat porous metals, complex shapes, and large objects after the device has been produced; 3) the ability to coat a wide variety of metals, alloys, ceramics, and plastics; and 4) potential choice for the type of mineral formed. Current applications of the biomimetic process include: a) coatings which protect the underlying substrate against physical and chemical attack; b) ultraviolet light-blocking coatings; c) magnetic films; and d) bioactive and biocompatible coatings for orthopedic implants. A license has been issued to Health Tech Development, Inc., of Dallas, Texas, for biomedical applications of the biomimetic process.

Publication

B.C. Bunker, P.C. Rieke, B.J. Tarasevich, A.A. Campbell, G.E. Fryxell, G.L. Graff, L. Song, and J. Liu. 1994. "Ceramic Thin Film Formation on Functionalized Interfaces Through Biomimetic Processing." *Science* 264:48.

Office of Basic Energy Sciences
Division of Materials Sciences

Biologically Inspired Coatings

Biomimetic[®] research concepts have resulted in an aqueous coating process. Unique advantages of this process include:

- A uniform coating on a wide variety of shapes and materials including porous surfaces
- An aqueous environment at temperatures less than 70°C
- The ability to control the phase of the deposited material

Because of these unique properties, this process has been used to deposit bioactive minerals on orthopedic implant devices. The bioactive coating minimizes implant rejection and maximizes the patient's rate of healing.

AA Campbell and GL Graff
Pacific Northwest Laboratory

Zircon as a Waste Form for the Permanent Disposal of Plutonium Recovered from Nuclear Weapons

Principal Investigators: W.J. Weber

R.C. Ewing, University of New Mexico

Funding Source: Office of Basic Energy Sciences, Division of Materials Sciences (KC-02)

As part of fundamental research over the past decade on the kinetics of irradiation effects in complex ceramics, studies involving natural zircon minerals of great geologic age, zircon containing 10 wt% plutonium, and ion-beam-irradiated zircon have resulted in a comprehensive understanding and detailed models of the mechanisms, processes, and effects of irradiation damage in zircon, particularly damage from the alpha decay of incorporated actinides, such as plutonium. The processes and critical parameters that control irradiation effects have been determined. Irradiation-induced changes in structure, volume, mechanical properties, stored energy, and dissolution rates have been determined as a function of cumulative dose over time periods ranging from minutes to 570 million years. Models of the effects of irradiation in zircon as a function of cumulative dose and temperature have been developed and verified by experimental results. The activation energies associated with the two simultaneous recovery processes in zircon during irradiation have been determined (0.02 ± 0.01 eV and 0.31 ± 0.03 eV) and shown to be independent of the irradiation-damage source.

One of the daunting new challenges facing the Department of Energy is to stabilize and dispose of excess weapons plutonium. A performance assessment based on the scientific results leads to the conclusion that

zircon is the most suitable waste form for the permanent disposal, in deep geologic formations, of plutonium recovered from the nuclear weapons program; furthermore, the technology could be ready for implementation within 2 years. The results of these studies demonstrate that 10 wt% plutonium can be incorporated into the zircon (ZrSiO_4) structure by partial substitution of plutonium for zirconium; crystal chemistry analysis further suggests that higher levels of plutonium incorporation is possible. Zircon is well established as an extremely durable mineral phase that is capable of retaining actinides for over 2 billion years. Based on the database and models developed under these studies, the performance of zircon in the geothermal gradient of a deep bore-hole under self-irradiation from the decay of plutonium (and uranium daughter product) can be reliably predicted over geologic time scales (billion years). Such a database and models do not exist for any of the other waste forms currently under consideration for plutonium disposal.

Publication

R.C. Ewing, W. Lutze, and W.J. Weber. "Zircon: A Host Phase for the Disposal of Weapons Plutonium." *J. of Materials Research* 10(2) (in press).

Basic Research Provides Technology for Weapons Plutonium Disposal

Office of Basic Energy Sciences
Division of Material Sciences

WJ Weber *Pacific Northwest Laboratory*
RC Ewing *University of New Mexico*

KC-03 Chemical Sciences

Design of Separation Materials: Molecular Dynamics Study of the Mechanism of Ion Selectivity of 18-Crown-6 Ether in Aqueous Solution

Principal Investigator: L.X. Dang

Funding Source: Fundamental Interactions Branch, Division of Chemical Sciences, Office of Basic Energy Sciences (KC-03-01-02-0)

Crown ethers have been proposed as separations agents for removing radioactive material, such as strontium-90 and cesium-137, from the mixed tank wastes at Department of Energy sites. A thorough understanding of the mechanism of selectivity of crown ethers for metal cations is needed to enable the development of improved separations agents. Toward this end, scientists in the Environmental Molecular Sciences Laboratory (EMSL) have performed extensive molecular dynamics simulations to examine the mechanism and thermodynamics for selectivity of 18-crown-6 ether for alkali ions in aqueous solutions. These simulations accurately reproduce the experimentally observed selectivity, and also provide a detailed physical description of the mechanism for ion selectivity in macrocyclic crown ethers. This research lays the groundwork for using molecular-level simulations of ion/macromolecular association in aqueous solutions to assist in the design of more efficient separations agents.

Molecular-level simulations are used in this project to reveal the physical factors that control the selectivity of macromolecules, such as crown ethers, for cations in aqueous solution. In addition, this research seeks to establish molecular-level simulations as a reliable tool to aid in the design of more efficient separations agents.

Efficient and highly selective separations agents are required to remove radioactive elements, such as strontium-90 and cesium-137, from mixed waste stored at DOE sites such as Hanford. The mixed wastes contain conventional wastes products, such as solvents, chelating agents, nitrates, salts, etc., as well as radioactive material. These diverse and highly variable mixtures present a major challenge for separations technologies. By separating radioactive materials from the low-level wastes, the volume of high-level wastes destined for expensive, long-term, deep-earth repositories can be greatly reduced, resulting in substantial savings in cleanup and storage costs.

Crown ethers have a long history of use as separations agents for positively charged alkali and alkaline earth metals in aqueous solution. The ether 18-crown-6, one of

the simplest examples of the cyclic, has been well studied experimentally and offers a convenient testing ground for molecular simulations techniques. In this work, effective potential energy profiles for fixed intermolecular separations of the ion and crown ether, obtained from averaging the intermolecular force over a statistical ensemble of solvent configurations (the so-called potential of mean force [PMF]), have been computed for $M^+ : 18\text{-crown-6}$ ($M^+ = K^+, Na^+, Rb^+, \text{ and } Cs^+$) complexation in water. Corresponding binding free energies have also been computed from these PMFs or free energy profiles. The resultant PMFs indicate that minima in the free-energy curves for K^+ and Na^+ are located at the crown ether center of mass. A well-defined second minimum is also observed in the PMF of the $Na^+ : 18\text{-crown-6}$ complex in water. It appears that K^+ is selected over Na^+ because of the greater free-energy penalty associated with displacing water molecules from Na^+ as it approaches the crown ether. This leads to a substantial increase in the activation free energy and a decrease in the corresponding binding free energy for $Na^+ : 18\text{-crown-6}$ complexation as compared to $K^+ : 18\text{-crown-6}$. The selection of K^+ over Rb^+ and Cs^+ is due to the size of the cation relative to that of the crown-ether cavity. The calculated binding free energies slightly underestimate the experimental measurements and correctly reproduce the experimental trends in the selectivity (e.g., $K^+ > Rb^+ > Cs^+ > Na^+$). The use of the PMFs not only allows the accurate reproduction of the experimental observations but also provides a detailed physical description of the mechanism for ion selectivity in macrocyclic crown ethers.

Publications

L.X. Dang and P.A. Kollman. "Free Energy of Association of the $K^+ : 18\text{-Crown-6}$ Complex in Water: A New Molecular Dynamics Study." *J. Phys. Chem.* 99 (in press).

L.X. Dang. 1995. "Mechanism and Thermodynamics of Ion Selectivity in Aqueous Solutions of 18-Crown-6 Ether: A Molecular Dynamics Study." *J. Am. Chem. Soc.* 117, 6954.

Snapshots of Cs^+ binding to 18-crown-6 ether in aqueous solution. Parts (a) and (b) are two views of the same configuration rotated by 90° . The atoms are labeled red for Cs^+ , green for Cl^- , blue for O, black for C, and white for H. The cyclic structure of CCO units in the center of part (a) is the 18-crown-6 ether binding the (red) Cs^+ ion. Waters of solvation in the first solvation shell around the crown ether and ions and the Cl^- counterion are also shown.

Potentials of mean force, part (a), and free energies, part (b), for binding of alkali cations to 18-crown-6 ether in aqueous solution.

High Level Ab Initio Study Reveals the Basis for Rapid Hydrogen Atom Transfer Between Ketyl Radicals and Ketones

Principal Investigators: J.A. Franz, D.M. Camaioni, and T. Autrey

Funding Source: Chemical Sciences Division, Free Radical Chemistry of Coal Program (KC-03-02-01-0)

Pacific Northwest Laboratory scientists applied advanced ab initio computational chemistry to reveal the structural basis for the rapid transfer of hydrogen atom from ketyl radicals to ketones. Ketyl radicals are a class of organic free radicals formed by removing a hydrogen atom from an alcohol (e.g., such as a ribose group in an RNA molecule), or by adding a hydrogen atom to a ketone (e.g., the carbonyl group of a cytidine molecule in DNA):

The question is, why does this reaction occur rapidly at room temperature such that it is potentially very significant in radiation damage and free radical reactions in cellular structures, when the analogous reaction with simple carbon-based reactions *does not occur*:

Advanced ab initio calculations utilizing Department of Energy supercomputing resources at Lawrence Livermore (Cray C-90) revealed that unlike the all-carbon system, the ketyl/ketone reaction proceeds through a unique transition state involving stabilization of the carbon centers through weak carbon-carbon bonding in a *syn* structure.

The activation barrier calculated at the PUMP2/6-31G** level was 16 kcal/mol for the simple formaldehyde plus ketyl radical model, compared with the much higher barrier, 28 kcal/mol, for the all-carbon system or 28 kcal/mol for the *anti* transition structure. More complex ketyl radicals and ketones will exhibit lower barriers.

The results of this study demonstrate that this reaction is quite facile and will act as an efficient hydrogen transfer mechanism in thermal processes such as coal liquefaction and lignin degradation. More importantly, it is clear that processes such as hydrogen transfer from sugar-based DNA free radicals to carbonyl groups in DNA will be very efficient, *providing the molecular ensemble can achieve the necessary syn-type complex* shown. This pathway is predicted to be important for hydrogen migration in radiation damage to biological structures.

With the present theoretical insights, studies of the kinetics and stereochemical limitations for hydrogen transfer between ketyl radicals and ketones is under way.

Publication

J.A. Franz, D.M. Camaioni, and T. Autrey. "Hydrogen Transfer From α -Hydroxy Methyl Radical to Formaldehyde: Ab Initio Methods Reveal *syn*-Like Transition State Stabilized by Weak Carbon-Carbon Bonding." *Journal of Physical Chemistry* (submitted).

High Pressure On-Line Photolysis with NMR Detection

Principal Investigators: C.R. Yonker and J.L. Fulton

Funding Source: Office of Basic Energy Sciences (KC-03-02-02)

High pressure nuclear magnetic resonance structural studies have been combined with laser photolysis to study the effect of pressure and temperature in the photoreversible ring closure reaction for a fulgide molecule (structure I)(see the figure). To our knowledge, this is the first time these techniques have been combined in this novel configuration. Studies of the fulgide molecule under pressures up to 3.0 kbar and temperatures of 120°C while undergoing laser photolysis was accomplished. Results showed a pressure stabilization of the fulgide (structure I) at 2.0 kbar and 120°C, in which ring closure to structure II did not occur. At 60°C the rate of formation of structure II during photolysis was decreased compared with the formation rate at 25°C. The results at 120°C were unexpected. It has been reported that at 1 bar and temperatures greater than 100°C, the ring closure to structure II readily occurs. Also, the formation of structure II was seen to be linearly dependent on laser exposure time and have a slight dependence on pressure. Future research efforts will entail trying to understand the pressure stabilization of the fulgide on a molecular level.

The combination of these techniques allows us to use pressure as a true thermodynamic variable to study its effect in photochemical reactions, obtaining structural and dynamic information about solution species from NMR. The experimental system allows the investigation of temperatures beyond the boiling point of the solute species due to the great pressures achieved in the capillary cell. This technique opens the area of pulse laser kinetic studies that occur on the NMR time scale to investigate cage effects as a function of pressure and temperature and could be important for the development of high pressure chemically induced dynamic nuclear polarization (CIDNP) techniques. The fulgide molecule is an ideal

molecule for an initial investigation of this type as the photoreaction of the conversion of structure I $\rightarrow$ II is linear with the photon flux. The longer the exposure time to the laser emission, the greater the amount of structure II formed. The effect of the photolysis of the fulgide at 25°C and 2 kbar can be seen in the figure, in which time lapsed high pressure NMR spectra are displayed. The bottom high pressure NMR spectra were taken ~90 minutes after the start of laser photolysis and the others follow at a time interval of ~105 minutes. The decrease of the methyl peak resonance at 0.84 ppm (R_3) corresponds to the decrease in structure I. The increases in the three methyl group ^1H resonances as a function of time are due to the photoconversion of I $\rightarrow$ II. These ^1H resonances in structure II correspond to, R_4 at 1.01 ppm, R_3 at 0.78 ppm, and R_2 at 0.55 ppm. In the closed ring system, the equatorial methyl group (R_4) is deshielded by the carbonyl on the anhydride group as compared with the axial methyl group (R_3). The two methyl ^1H resonances R_1 and R_5 , which are not presented in the figure show slight upfield shifts. Thus, the photoconversion of I $\rightarrow$ II shows the largest chemical shift changes on ring closure for the methyl ^1H resonances of groups R_4 and R_2 , which shift from 1.85 $\rightarrow$ 1.01 ppm and 2.07 $\rightarrow$ 0.55 ppm, respectively. The reason for this large change in chemical shift is due to the change in conjugation of structure II upon ring closure in which both groups are more shielded than in the fulgide structure.

Publication

C.R. Yonker and S.L. Wallen. "High-Pressure On-Line Photolysis With NMR Detection." *Journal of Applied Spectroscopy* (submitted).

**Structure of the fulgide (I) and the photochromic product (II).
R, represents methyl groups on the molecule.**

Pacific Northwest Laboratory

Time series of high pressure NMR spectra at 2.0 kbar and 25C following the conversion of structure I to II. The first spectra was taken 90 minutes after the start of laser photolysis, the following spectra were taken 105 minutes apart from bottom to top.

Pacific Northwest Laboratory

Kinetic Free Energy Relationship Reveals Details of Strong Carbon-Carbon Bond Cleavage Reactions on Nanometer Scale Iron Sulfide Coal Liquefaction Catalysts

Principal Investigators: T. Autrey, J.C. Linehan, D.M. Camaioni, and J.A. Franz

Funding Source: Chemical Sciences Division, Free Radical Chemistry of Coal Program (KC-03-02-01-0)

Pacific Northwest Laboratory scientists uncovered new detailed pathways of hydrogen donation and hydrocracking of strong carbon-carbon bonds by novel nanometer iron sulfide (FeS) catalysts. Diarylmethanes ($\text{Ar-CH}_2\text{-Ar}$, Ar = aromatic ring, e.g., benzenoid structure) represent an important class of nearly inert linkages in coal structure. Successful catalytic hydrogenolysis of coal and upgrading of petroleum resid requires the efficient cleavage of these bonds. Among many published studies of reactions of FeS catalyst reactions, this was the first to provide meaningful mechanistic data and insight into reactive hydrogen donating intermediates on the catalyst surface. Samples of the catalyst and versions of the catalyst doped with molybdenum and nickel are presently being examined for their utility in industrial-scale upgrading of petroleum resids.

The significance of this study was to provide coal science and chemistry in general with a predictive, quantitative mechanistic description of detailed free radical pathways of bond scission involving the important class of iron catalysts. The insights of this study point to a category of FeSH structures which now can be prepared for detailed modeling of the reactive catalytic species. The reactivity and selectivity of FeS catalysts can thus be modified and optimized.

By application of a Bell-Evans-Polanyi treatment of the relative rates of cleavage of different aromatic structures ($\text{Ph-CH}_2\text{Ar}$, where Ar = $\text{C}_6\text{H}_4\text{CH}_3$, $\text{C}_6\text{H}_3(\text{CH}_3)_2$, $\text{C}_6\text{H}_2(\text{CH}_3)_3$, and others), the reactivity of the surface SH group responsible for bond cleavage was determined. It was found that for each kcal/mol of increased stability of the hydroaryl radical intermediate, the activation barrier

for bond cleavage was reduced by 1 kcal/mol, (e.g., a late transition state best represented by the reaction of two closed-shell structures to give two free radicals, one on the catalyst surface and one from the diarylmethane model compound). A novel ferrihydrite catalyst precursor prepared by the group is converted in situ to an "FeS" catalyst which, in the presence of a hydrogen source, successfully cleaves the nearly inert diarylmethane structures. By measurement of the kinetics of cleavage of a family of substituted phenylarylmethanes, free radical pathways were indicated. The Bell-Evans-Polanyi type correlation revealed bond cleavage to occur by reaction of a Fe-S-H-like group directly adding the H to the aromatic ring of the molecule undergoing cleavage to produce two free radicals (a reverse-radical-disproportionation, RRD, reaction). One of the two radicals rapidly cleaves, giving the desired strong carbon-carbon bond cleavage reaction.

With the new insight into active site structure of the FeS catalyst, work to synthesize homogeneous organometallic models of the reactive intermediates is under way to determine and compare reactivities of organometallic model structures toward hydrogen donation and hydrocracking.

Publication

T. Autrey, J.C. Linehan, D.M. Camaioni, J.A. Franz, L.E. Kaune, and H.W. Watrob. "Mechanistic Investigations of Iron/Sulfur-Catalyzed Bond Scission in Aromatic Hydrocarbons. A Catalytic Hydrogen Transfer Step Involving a Late Transition State." *Catalysis Today* (in press).

Laser Interactions with an Ionic Molecular Crystal: Sodium Nitrate Ablation in the 6-eV Valence Band

Principal Investigators: R.A. Bradley Jr., E.J. Lanzendorf, M.I. McCarthy, T.M. Orlando, and W.P. Hess

Funding Source: Strategic Environmental Research and Development Program (KC-03)

Laser ablation is an important technique in an increasing number of fields including chemistry, physics, materials science, microelectronics, biology, and medicine. The utility of laser ablation is derived from the diversity of materials that are amenable to the technique. Laser ablation combined with mass spectrometry (LAMMS) is being developed as a diagnostic tool for analysis of atomic and molecular species in mixed hazardous wastes. Using this approach, complex multicomponent mixtures can be analyzed rapidly using very little sample. Reduced sample size is highly desirable for the analysis of many hazardous wastes because it minimizes the secondary waste generated from the analytic procedures and exposure of laboratory workers to larger volumes of hazardous waste. The LAMMS technique is being applied to analyze mixed wastes extracted from the underground storage tanks at Hanford. A major component of these tanks is sodium nitrate (NaNO_3), so understanding the ablation mechanisms of this material is essential to analyzing these wastes. Sodium nitrate is a wide-band-gap, insulating material that forms a molecular ionic crystal with a hexagonal unit cell of D_{3d} symmetry. We have examined laser/solid interactions following resonant excitation of single-crystal sodium nitrate by measuring the translational, rotational, and vibrational energy distributions of desorbed NO.

The neutral NO desorption yield is quantitatively different for resonant excitation of the band at 213 nm as compared to nonresonant excitation at 266 nm. For freshly cleaved samples, the neutral NO yield for 213-nm excitation is approximately 1000 times greater than for 266-nm excitation, hence it is clear that resonant excitation leads to a significant enhancement of the NO yield due to a photochemical reaction. Examination of the power dependence of the ablation process indicates that all NO production is a result of single-photon absorption at 213 nm.

For the NO desorbing from the surface, there is significant population in the higher vibrational states. This vibrational distribution provides a poor fit to a Boltzmann plot, and must therefore be nonthermal. The time-of-flight spectra are fit to a half-range Maxwell-Boltzmann velocity distribution function, yielding a translational

temperature of 250 ± 40 K, in thermal equilibrium with the unirradiated surface. We have also investigated the rotational energy distribution of the desorbing NO from NaNO_3 ablation at 213 nm. A Boltzmann analysis of the spectrum yields a rotational temperature of 270 ± 50 K for the ablated NO. Data obtained at higher temperatures indicate that the rotational temperature of the desorbing NO tracks with the substrate temperature. The observation of considerable NO vibrational excitation implies that the surface residence time of the newborn NO product is short compared with the lifetime of vibrationally excited NO on the surface. This may be due to the poor energy match between a vibrational quantum for NO with the Debye frequency of crystalline NaNO_3 . The translational and rotational state distributions however, indicate a finite residence time as these degrees of freedom are equilibrated with the surface temperature.

The surface dynamics of photoexcited NaNO_3 results from the dissociation of the NO_3^* exciton at or near the surface. Since this exciton presumably self-traps at the vacuum surface interface, the subsequent dissociation mechanisms can be described in terms of the decay of a surface-bound negative ion excited state. Hence, the ablation process is actually probing the *photochemistry* of the NaNO_3 solid-to-gas interface.

Publications

R.A. Bradley Jr., E. Lanzendorf, M.I. McCarthy, K. Peterson, T.M. Orlando, and W.P. Hess. "Laser Interactions with an Ionic Molecular Crystal: Sodium Nitrate Ablation in the 6 eV Valence Band." *J. Phys. Chem.* (in press).

K. Knutsen and T.M. Orlando. "Low-Energy (10–80 eV) Electron-Stimulated Desorption of $\text{H}^+(\text{D}^+)$, $\text{OH}^+(\text{OD}^+)$, and Na^+ from Solution Grown NaNO_3 Crystals." *Surf. Sci.* (submitted).

A. Peurrung, J.P. Cowin, S.E. Barlow, G. Teeter, and T.M. Orlando. "Space-Charge Induced Acceleration of Ions Emitted by Laser-Irradiated Surfaces." *J. Appl. Phys.* (submitted).

LASER INTERACTION WITH AN IONIC MOLECULAR CRYSTAL: SODIUM NITRATE ABLATION

- Laser ablation/ mass spectrometry is being developed as a diagnostic for the analysis of mixed hazardous wastes.
 - rapid, inexpensive
 - minimizes secondary wastes
- Ablation of NaNO_3 (a major component of tanks) is essential to understanding the analytical process.
- Detailed observations have clarified the mechanics of the process:
 - resonant excitation greatly enhances the NO yield
 - NO production results from a single-photon excitation at 213 nm
 - vibrational distribution is nonthermal
 - rotational temperature tracks with substrate temperature
 - surface residence time of NO product is short
- The ablation process probes the photochemistry of the NaNO_3 solid-to-gas interface.

NaNO₃ Abalation Mechanism

Characteristics of Laser Ablation

Rapid Laser Heating

Material and λ dependent
Metal free electron excitation
Multiphoton absorption
Valence excitation

For an irradiance of $3 \times 10^8 \text{ W/cm}^2$ on Cu metal
Then $\Delta T = 2000 \text{ K}$ in 10 ns

Laser Pulse

$$\Delta T (\text{K}) = I_0 \cdot \tau / \sqrt{\kappa \cdot \tau} \cdot \rho \cdot C_p$$

Sample

Modeling of Environmental Molecular Systems: The Development of Hybrid Quantum Mechanical/Molecular Mechanical Methods with Polarization

Principal Investigators: M.A. Thompson and G.K. Schenter

Funding Source: U.S. Department of Energy Cooperative Research and Development Agreement (CRADA) PNL050 in conjunction with E.I. DuPont de Nemours Inc. and Fundamental Interactions Branch, Division of Chemical Sciences, Office of Basic Energy Sciences (KC-03-01-02-0)

Modeling of complex molecular processes in environmental systems holds the promise of yielding fundamental information that will greatly increase our understanding of these systems and thereby improve our ability to provide new solutions to existing environmental problems. A major challenge is the accurate description of very large molecules that occur in natural and contaminated systems such as macromolecules used to separate radionuclides from tank wastes (e.g., crown ethers), biomolecules proposed for redesign to assist bioremediation of contaminated soils (e.g., enzymes), and complex organic compounds found in soils and groundwater (e.g., humic material). A second challenge is to develop models that will provide an understanding of fundamental molecular processes in the condensed phase through the interpretation of spectroscopic probes.

We have developed a technique that accurately describes the influence of the surrounding environment on excited state spectroscopic processes and is robust enough to describe large and complex systems. Since the early days of theoretical quantum chemistry, the interpretation of electronic spectra has been a primary goal, but most quantum mechanical studies have been limited to isolated molecules in the gas phase. Most experimental studies involve molecules in complex environments, such as in solution where the spectroscopy of the isolated molecule is significantly altered through interactions with the surrounding medium. This interaction is so significant that the comparison of condensed phase spectra to its isolated molecule counterpart provides a useful probe of the local molecular environment. It is a goal of this work to better understand this relation.

Our technique involves separating the system into a quantum mechanical (QM) component where the explicit electronic excited state structure is considered in determining interactions, and a molecular mechanics (MM) component where interactions are described in terms of empirical terms with physical meaning such as van der Waals and static coulomb interactions. The introduction of a

polarization response of the medium in addition to a static coulomb interaction (MMpol) provides a description of the system that is more consistent with the QM treatment and represents a significant accomplishment of this work.

As a characteristic system, we studied the electronic excited states of the photosynthetic reaction center of the photosynthetic bacteria *Rhodospseudomonas viridis*, with the goal of understanding the asymmetry associated with the primary charge separation. The initial events of photosynthesis involve a light-driven charge separation across a photosynthetic membrane. The mechanism of this primary charge separation remains elusive, but it is observed to be asymmetric. Electron transfer proceeds only along the L branch, not the M branch. To model this system, we considered the electronic quantum mechanics of 325 atoms that contained the "special pair" or primary donor, P, in the presence of the field of 20,158 polarizable molecular mechanics atoms. The explicit treatment of the protein interaction is required to explain the charge transfer asymmetry as measured by Stark effect experiments. The Stark angle is the angle between the difference in dipole moments of the excited and ground states and the transition moment, and reflects the asymmetry of the reaction center. This angle has been experimentally determined to be 37°. If we consider the QM system alone, we recover an angle of 89°; by including static molecular mechanics interactions, we recover an angle of 54°. The inclusion of polarization (MMpol) reduces the angle to 43° to give a better agreement with experiment, reflecting the asymmetry induced by the surrounding protein environment.

Publication

M.A. Thompson and G.K. Schenter. 1995. "Excited States of the Bacteriochlorophyll b Dimer of *Rhodospseudomonas viridis*: A QM/MM Study of the Photosynthetic Reaction Center That Includes MM Polarization." *J. Phys. Chem.* 99, 6374.

Development of a Quantum Mechanical/Molecular Mechanics with Polarization model for microscopic solvation (QM/MMpol)

The Excited State Spectroscopy of the Bacteriochlorophyll b Dimer (P) of the photosynthetic reaction center (RC) of *Rhodospseudomonas viridis*.

Mark A. Thompson and Gregory K. Schenter, J. Phys. Chem. 99, 6374 (1995)

- 325 QM atoms embedded in the field of 20158 polarizable MM atoms.
- QM allows an accurate description of the ground and excited electronic states using a semiempirical electronic structure method such as INDO/S.
- MMpol provides a representation of the interaction of the surrounding medium, the protein, on the QM system. The inclusion of a polarization response of the medium in addition to a static coulomb interaction provides a description that is more consistent with the QM treatment.
- The mechanism of primary charge separation remains elusive. Electron transfer proceeds only along the L branch, not the M branch. The explicit treatment of the protein interaction is required to explain the charge transfer asymmetry as measured by Stark effect experiments.
- Stark Angle (angle between $\mu_e - \mu_g$ and the transition moment μ_{eg})

<u>MMpol</u>	<u>QM Experiment</u>	<u>QM/MM</u>	<u>QM/</u>
37°	89°	54°	43°

Bacterial Photosynthetic Reaction Center from *Rhodospseudomonas viridis*

Modeling of Environmental Molecular Systems: Quantum Mechanical Simulations of Aqueous Ionic Clusters

Principal Investigators: H. Gai, L.X. Dang, G.K. Schenter, and B.C. Garrett

Funding Source: Fundamental Interactions Branch, Division of Chemical Sciences, Office of Basic Energy Sciences (KC-03-01-02-0)

Molecular processes occurring in aqueous solutions play an important role in many environmental systems. For example, the speciation and reaction of molecules in the aqueous solutions of waste tanks influence the behavior of the tanks, such as their ability to generate hydrogen; the solubility and reactivity of molecules in groundwater control the transport and transformation of contaminants through the subsurface; and the uptake and subsequent reaction of molecules by aqueous droplets and aerosols in the atmosphere greatly influence concentrations of chemicals such as ozone in the troposphere. Molecular modeling of complex environmental systems holds the promise of yielding fundamental information that will greatly increase our understanding of these systems and thereby improve our ability to provide new solutions to existing environmental problems. Reliable modeling of molecular processes in the environment requires accurate descriptions of the potential energies of interaction between molecules. The goal of this research is the development of accurate interaction potentials and a greater understanding of the important factors that need to be included in these interaction potentials.

Most models of potential energies for water-water interactions, which are needed to model molecular processes in aqueous solutions, have been developed to reproduce experimental properties of the bulk liquid. These models generally make approximations to the water molecule to reduce computational requirements. For example, most interaction potentials treat water as a rigid molecule with fixed charges on the atoms. Physical effects, such as vibrations of the molecule and charge redistribution within water in solution, are included in an average sense to reproduce the empirical data for the bulk liquid. These models will fail when local environments of the aqueous solution require the behavior of individual water molecules to deviate significantly from their average bulk properties. For example, the ionization of an acid in water will require both the structure and charge distribution of water molecules near the acid to change radically to accommodate the proton.

Another limitation of these empirical interaction potentials is that they are developed so that classical simulations of the molecular motion reproduces the empirical data. For systems containing hydrogen atoms, the classical approximation to the true quantum mechanical dynamics is often not adequate. In these cases, the empirical models account for these quantum mechanical effects in an average sense. To date, there have been very few studies of the importance of quantum mechanical effects in modeling aqueous solutions.

In this research, classical and quantum (Path Integral Monte Carlo) simulations are performed at three temperatures (i.e., 100, 200, and 300 K) on the ionic clusters $\text{Cl}^-(\text{H}_2\text{O})_n$, $n=1-6$, to determine the importance of quantum effects on nuclear motion. To the best of our knowledge, this is the first application of the nuclear quantum mechanical approach to the evaluation of energetic and structural properties of the ionic clusters. Polarizable water-water and ion-water interaction potentials are used. The enthalpies for binding water molecules to the ion are computed both classically and quantum mechanically. The difference between the classical and quantum results are most significant at lower temperature (i.e., at 100 K) where the difference can amount up to 20% of the total energy. Although the binding enthalpy curves for a given temperature can be reproduced using classical simulation by adjusting the interaction potential, the temperature dependence of these curves cannot. Thus, we see that when an accurate description of the temperature dependence of these systems is needed, the quantum mechanical effects must be treated.

Publication

H. Gai, L.X. Dang, G.K. Schenter, and B.C. Garrett, "Quantum Simulation of Aqueous Ionic Clusters." *J. Phys. Chem.* (in press).

The difference in enthalpy of binding between classical and quantum simulations, $\Delta H_{\text{Quantum}} - \Delta_{\text{Classical}}$, as a function of numbers of water molecules in $\text{Cl}^-(\text{H}_2\text{O})_n$ clusters.

Molecular Dynamics at the Water/Solid Interface

Principal Investigators: M.J. Iedema, S.A. Joyce, H. Wang, J. Biesecker, N. Kizhakivariam, and J.P. Cowin
Funding Source: Office of Basic Energy Sciences (KC-03)

Defects at oxide surfaces can control the chemistry of many reactions and mediate contaminant transport in soils. To explore the effect of defects, we have studied the adsorption/desorption kinetics of water on thin single-crystal films of MgO [on a Mo(100) surface]. Scanning tunneling microscope studies show that several-monolayer MgO films grow nearly atomically smooth, but have domain sizes that range from about 20 Å for an unannealed film grown at 400 K, to 150 Å after annealing at 1050 K. The fraction of sites bordering the edges of the domains should range from 10% to 50% in these two cases. Water desorption on these surfaces shows that there are two contributions to the binding/desorption of water that scale roughly in proportion to the expected fraction of edge atoms. When the thin film is grown on a 4.5° tilted (thus stepped) substrate, the water desorption on the stepped oxide also shows the effect of having more defect sites. New work in progress uses atomic epitaxy of an intimately mixed oxide, CaO + MgO, to explore the effect of substitutional defects on water chemistry on an oxide surface.

Much of the chemistry of importance in aqueous-mineral and electrochemistry involves aqueous ions. Our studies of ions at surfaces involve a collaboration between Pacific Northwest Laboratory and the University of Colorado.

Professor Barney Ellison and his student John Biesecker built an ion source and delivered it to PNL for joint use. We are using cryogenic temperatures (≤ 20 K) and molecular beam dosing to create models of aqueous interfaces with known spacing between various molecules, ions, and the surface. Unlike others, we employ a mass-selected, positive or negative molecular-ion beam, producing 10 to 50 nA of ions at several eV impact energy. This technique enables us to study ionic surface processes for a wide range of molecular ions (NH_4^+ , H_3O^+ , N_2O^+ , NO_3^- , ClO^- , CN^- , OH^- , etc.). We can prepare systems at equilibrium or ones which are highly metastable. Neutralization of the deposited ions makes it an effective radical source. These capabilities also allow studies of important atmospheric chemistry of aerosols for species like ClO, ClO^- , and $\text{NO}_x^{+/-}$.

The source was recently demonstrated for (N_2O^+) narrow-energy beams at 10 nA or higher fluence, at an impact energy of about 1 V. As the beam energy is reduced from 500 V, the current is nearly constant down to the 1-V limit. Previous attempts by others have shown strong beam losses typically starting below 50 V. Our design minimizes these losses, which are due to space-charge effects. Hydration and ion migration studies are under way using thin-layer water epitaxy plus ions.

Molecular Ion Deposition

(with Prof. B. Ellison, Univ. Colorado)

NH_4^+ , OH^- , H^+ , H_3O^+ , Fe^{2+} , HCO_3^- , Cl^- , etc.

RECREATE AQUEOUS ION ENVIRONMENTS VIA PRECISE EPITAXY

Surface Defect-Chemistry of Oxides: MgO + Water

Scanning Tunneling Microscope Studies of MgO/Mo Thin Films

Room Temperature Growth
Small domains (30-60Å)
40% edge site defects

Post Growth Anneal to 1100K
Larger domains ~150Å size
< 10% edge site defects

Single-Molecule Spectroscopy and Dynamics at Interfaces

Principal Investigators: X.S. Xie, R.C. Dunn, E.V. Allen, G.R. Holtom, and G.A. Anderson
Funding Source: Office of Basic Energy Sciences (KC-03)

Recent advances in near-field optical and fluorescence microscopy make it possible to conduct single-molecule spectroscopy at the nanometric scale in an ambient environment. The instrumentation employs an optical fiber that has been pulled to very small diameter and coated, leaving a sharp tip with an approximately 20-nm opening, roughly the size of a single protein molecule. This fiber is mounted as a replacement tip in an atomic force microscope (AFM), and is operated as an AFM to obtain a topographic image of the sample, which is simultaneously excited with light emanating from the fiber tip; induced fluorescence is detected and analyzed to obtain an optical image at 5 to 10 times the resolution obtained with existing optical microscopes. This instrumentation was developed in a collaboration between Environmental Molecular Sciences Laboratory scientists and their colleagues at Digital Instruments. It has provided for the first time unprecedented and detailed information on topography, optical spectra, and lifetimes of single protein complexes and other molecular species in intact photosynthetic membranes, and of single molecules on mineral surfaces, and has promising applications to biological, environmental, and materials sciences.

In using time-resolved single-molecule spectroscopy to chemical reactions on individual molecules, there are two classes of time-resolved experiments: On the 10^{-2} to 10^{-3} second time scale, one can observe single events, such as orientational motions, spectral diffusion, and photobleaching. Single-molecule events are usually characterized by abrupt jumps in experimental observables. For example, we have observed intensity fluctuations in the emission from single sulforhodamine 101 molecules dispersed on a glass surface, which are attributed to spectral diffusion (instead of rotational diffusion) of the molecules. On the picosecond to nanosecond time scale, one can study the dynamics of repetitive processes, making it possible to study photo-induced chemical reactions of single molecules in specific local environments. The fluorescence

decay of a single oxazine 725 molecule dispersed on a glass surface has been observed. This molecule undergoes a twisted intramolecular charge transfer reaction on its excited state. Interestingly, we find a distribution in the charge transfer rates for individual molecules. Time-resolved fluorescence measurements on a single-molecule basis allow us to study chemical reactions at interfaces with much greater detail than has heretofore been possible.

Publications

R.C. Dunn, E.V. Allen, S.A. Joyce, G.A. Anderson, and X.S. Xie. 1995. "Near-field Fluorescent Imaging of Single Proteins." *Ultramicroscopy* 57, 113.

L.S. Wang, J. Fan, X.S. Xie, E.V. Allen, G.R. Holtom, R.C. Dunn, and L. Mets. 1994. "Near-Field Fluorescence Microscopy and Spectroscopy: Applications to Single Chromophores, Single Proteins and Photosynthetic Membranes." *Proc. SPIE 2137 (Time Resolved Laser Spectry. in Biochem. IV)*, 264.

X.S. Xie and R.C. Dunn. 1994. "Probing Single Molecule Dynamics." *Science* 265, 361.

X.S. Xie and R.C. Dunn. "Near-Field Single Molecule Spectroscopy." *Proc. SPIE 2385 (Advanced Optical Methods for Ultrasensitive Detection [in press])*.

X.S. Xie, and R.C. Dunn. "Single Molecule Microscopy and Spectroscopy." *Zoological Studies* (in press).

X.S. Xie, G.R. Holtom, L. Mets, and R.C. Dunn. 1994. "Near-Field Time-Resolved Spectroscopy on Single Molecules and Photosynthetic Membranes." *Ultrafast Phenomena IX* (Springer-Verlag), p. 124.

Near-field Optical Microscope

Nanometric Resolution
provides the ability
to resolve the spectroscopy
and dynamics
of single molecules.

Chemical Structure & Dynamics,
Pacific Northwest Laboratory

Single Sulforhodamine 101 Molecules Dispersed on a Glass Surface

The Journal of Physical Chemistry

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**Toward a Spectroscopic Mapping
of Photosynthetic Membranes**
(see page 3096)

PUBLISHED WEEKLY BY THE AMERICAN CHEMICAL SOCIETY

Structure and Reactivity of Ice Surfaces and Interfaces

Principal Investigators: C. Huang, E.K.L. Wong, R.S. Smith, and B.D. Kay
Funding Source: Office of Basic Energy Sciences (KC-03)

Molecular beam scattering from surfaces is a powerful experimental tool for studying the dynamics and kinetics of the interaction of molecules with surfaces. The coupling of surface science, molecular beam, and laser technologies makes possible the measurement of total energy disposal and redistribution in gas-surface scattering. Previously these experimental methods have been employed to acquire detailed surface kinetics and state-to-state scattering measurements of molecules interacting with metallic substrates. Such experiments have resulted in a fairly detailed understanding of surface chemistry on metals, but we currently do not have a similar understanding of the elementary dynamical and kinetic processes occurring on ice and oxide surfaces. Such interactions are clearly important from an environmental viewpoint, since they form the molecular-level basis for the complex physicochemical processes that take place on the surface of atmospheric aerosols, at the aqueous-mineral geochemical interface, and at the vapor-liquid interface. Our goal is to apply and extend molecular beam surface scattering techniques to these systems in an effort to elucidate the relevant interactions.

Our initial efforts have focused on the synthesis of thin films of H_2O and D_2O ice grown on Au(111) and Ru(0001) substrates. Using a molecular-beam-reflection technique, we have determined that the sticking coefficient is unity and independent of incident angle for surface temperatures below 130 K. Above 130 K the condensation coefficient decreases due to the onset of desorption but the trapping probability remains near unity. This is the first *direct* measurement of the condensation coefficient of gaseous water on ice surfaces. Previous indirect techniques have yielded conflicting values between 0.01 and 1 for the sticking coefficient. We have shown that

the condensation coefficient is dependent upon both flux and substrate temperature. The temperature and flux dependence of the condensation coefficient combined with naive kinetic models is the source of previous confusion regarding the value of the water-sticking coefficient on ice.

At temperatures below 140 K the initial water deposited forms a vitreous solid phase that is metastable with respect to crystalline ice. The existence of this metastable phase has been known for a long time, but the rate and mechanism by which it crystallizes is not understood. By an extensive series of careful desorption measurements (both temperature-programmed and isothermal) we were able to study the attendant crystallization kinetics quantitatively. The desorption kinetics are extremely sensitive to this phase transformation. To our knowledge, this is the first time such a transition has been observed in desorption. We observe a large isotope effect in the crystallization rate, with H_2O having a faster rate. Interestingly, the temperature-programmed desorption spectra for films grown on gold and ruthenium appear surprisingly similar. However, isothermal measurements clearly indicate that the desorption kinetics are substrate-sensitive. In contrast to conventional wisdom, the desorption kinetics exhibit marked departures from zero-order behavior.

Publication

R.J. Speedy, P.G. Debenedetti, C. Huang, R.S. Smith, and B.D. Kay. "The Entropy of Glassy Water." In *Proceedings of 12th International Conference on the Properties of Water and Steam*, Orlando, Florida, September 12-16, 1994. Begell House (in press).

"Molecular Volcano"

Amorphous to Crystalline Phase Transition Kinetics

As the amorphous ice crystallizes, the grain boundaries form a connected percolation path enabling escape of the underlying CCl₄.

Pacific Northwest Laboratory, EMSL, CS&D.

STRUCTURE AND REACTIVITY OF ICE SURFACES AND INTERFACES

- Basic investigation into surface chemistry important in environmental chemical processes.
- First *direct* measurements of condensation coefficient of water vapor on ice surfaces: sticking coefficient depends upon both flux and substrate temperature.
- Desorption measurements clarify crystallization kinetics: the first observation of a metastable phase transition in desorption.
- Studies of desorption impeded by a water overlayer reveal the "molecular volcano," a new phenomenon in amorphous-to-crystalline transition kinetics.

Water/Mineral Interfaces in Subsurface Transport: Chemistry at the Water/MgO Interface

Principal Investigators: M.I. McCarthy and M.R. Chacon-Taylor

Funding Source: Fundamental Interactions Branch, Division of Chemical Sciences, Office of Basic Energy Sciences (KC-03-01-02-0)

Understanding the chemistry and physics at water/mineral interfaces is crucial for deriving accurate models of the transport of contaminants through the subsurface. Scientists in the Environmental Molecular Sciences Laboratory have used state-of-the-art theoretical methods to probe the molecular-scale processes that control contaminant transport and transformation. Models based on in-depth investigations of selected systems are used to predict the nature of complex, naturally occurring minerals. The ultimate goal of this effort is to elucidate the links between molecular-scale interfacial phenomena and contaminant plume observables.

Contaminated soils and groundwater are one of the most recalcitrant remediation problems facing the Department of Energy. Water is ever present in the environment and can have a variety of interactions with exposed oxide surfaces, each of which will have a different effect on soil chemistry and on the transport of other chemicals through soils. Therefore, understanding the processes of water adsorption and chemical dissociation on oxide surfaces is fundamental to modeling subsurface transport phenomena. The *transport* of a contaminant through the subsurface environment is determined largely by its solubility in aqueous solution, its interaction with other molecules in the groundwater, and its interactions with soil materials, especially mineral surfaces. The *transformation* of contaminants in the subsurface environment is largely controlled by chemical reactions, occurring either in solution or at interfaces of aqueous solutions with mineral surfaces.

Materials that are known to greatly influence soil chemistry include clay minerals, zeolites, and certain metal oxides and oxyhydroxides. Magnesium oxide (MgO) is a structurally simple cubic oxide material. Its interfaces play an important role in subsurface geochemistry, catalysis, and materials design. The bulk, surface, and interface properties of MgO are being studied to understand the behavior of MgO and to derive models that can be used to model processes involving more complex oxides. The composition and structure of MgO make this a "computationally practical" system that can be studied in detail using ab initio electronic structure theory.

EMSL scientists have examined the molecular-scale details of the water/MgO interface. A fundamental question probed in this work is "What properties of a material—structural, electronic, magnetic, thermal, physical, and photochemical—determine the chemical reactivity of its surfaces?" In addition, it is necessary to determine the properties of realistic surface sites (containing point defects, steps, kinks) in order to quantitatively predict surface chemistry. Ab initio quantum mechanical investigations of the MgO/water interface examined the effect of defect sites on the surface chemistry. The calculations were done using a state-of-the-art computational method based on periodic Hartree-Fock theory. The calculations examined the behavior of water on clean and defected MgO (001) surfaces.

In particular, they addressed the question "Does water bind and/or dissociate on this surface?" The chemisorption pathway causes the surface to become "hydroxylated";

where the OH (hydroxyl) binds to surface magnesium sites and the hydrogen binds to surface oxygens. The calculations revealed that molecular water is weakly bound (~15 kcal/mol) to the clean surface, but dissociation of the water molecules is energetically unfavorable on the "perfect" surface. However, the computed energetics clearly indicate defects play a significant role in determining the chemical reactivity of this material. Water is more tightly bound to the corners (~26 kcal/mol) and edges (~20 kcal/mol) of a defect step and dissociation is energetically favorable on these sites (15 kcal/mol on edges and 72 kcal/mol on corners). This indicates that the interfacial properties of this mineral will vary depending on the number density of surface defects. The dissolution of this material will also be dependent on the surface topology.

A new methodology was also developed to derive electrostatic models of oxide interfaces. These models are constructed from the energetics of an adsorbate—described

by a multipolar expansion of the charge density—interacting with the quantum mechanical electric fields generated by the surface. This electrostatic model produces a reliable computationally "trivial" method for examining the properties of a range of interfaces. The results have been validated by comparing the classical data to quantum mechanical calculations on several systems. Excellent agreement was found between the computed electrostatic energetics and the quantum mechanical values for HCl, H₂O, and NH₃ on MgO. This approach provides us with a quantitative interpretation of

the interfacial bonding interactions that allow us to predict the properties of more complex materials with low symmetry.

Publication

M.R. Chacon-Taylor and M.I. McCarthy. "Comparison Between the Classical Interaction Energy and Periodic Hartree-Fock Binding Energies for the Interaction between Molecules and Surfaces." *J. Chem. Phys.* (in press).

Corner Defect

Edge Defect

Structural models used in the simulations of water adsorption at low coordinated binding sites. Blue spheres are oxygen ions, red spheres are magnesium ions and water is shown in green.

X-Ray Absorption Fine Structure of Solutes in Supercritical Water

Principal Investigators: J.L. Fulton and C.R. Yonker

Funding Source: Office of Basic Energy Sciences (KC-03-02-02)

Supercritical water oxidation has enormous potential for hazardous waste destruction. Due to the difficulty of experimentally probing this extreme solvent environment there is a severe lack of fundamental solvation information for this solvent. Scientists at Pacific Northwest Laboratory conducted the *first* XAFS (X-ray Absorption Fine Structure) study of supercritical water at the National Synchrotron Light Source at Brookhaven.

The XAFS technique is a powerful method to look at a local solvent environment in terms of the number of nearest solvent neighbors and hydration distance. PNL scientists successfully measured the degree of hydration of two cations, rubidium and strontium, and of an atomic solute, krypton, under supercritical water conditions. XAFS provides a direct measurement of the radial distribution function for water around the solutes and hence will be extremely useful for testing simulations and thermodynamics of this system. In simpler terms information was obtained on the differences in the number of waters-of-hydration around these cations as well as the changes in the nearest neighbor distances. For strontium in supercritical water, at a temperature of 385°C and a density of

0.54g/cm³, the number of waters-of-hydration was a factor of 0.52 of the number in liquid water under ambient conditions. To a first approximation, the number of hydrating water molecules is proportional to the fluid density. The radius of the first solvation shell changes very little at these elevated temperatures. Information of this type is virtually nonexistent and has made it difficult to develop reasonable models for supercritical water solvation dynamics.

Publications

J.L. Fulton, D.M. Pfund, and Y. Ma. "A Diamond Window XAFS Cell for Studies of High-Temperature, High-Pressure Aqueous Solutions." *Review of Scientific Instrumentation* (submitted).

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KC-04 Engineering and Geosciences

Structure and Reactivity of Ferric Oxide and Oxyhydroxide Surfaces

Principal Investigators: J.R. Rustad and A.R. Felmy

Funding Source: Office of Basic Energy Sources, Geosciences (KC-04-03)

The objectives of this program are to 1) develop the capability to create molecular models of hydroxylated ferric oxide and oxyhydroxide surfaces, 2) use these models to better understand the relationship between surface structure and reactivity for this class of minerals, and 3) use this knowledge to improve thermodynamic calculations using surface complexation models.

Ferric oxides have high specific surface areas, high affinities for oxyanions and heavy metals, and actively respond to changes in redox conditions in natural environments. These minerals are therefore important in a variety of low-temperature geochemical processes, particularly those in which adsorption and dissolution couple with fluctuations in redox potential. For many solutes, measurement of sorption density versus aqueous concentration suggests the presence of a heterogeneous array of surface sites having a range of affinities for the probing solute. Crystallographic differences in coordination and geometrical pattern of surface oxide sites are a fundamental aspect of this heterogeneity. In this project, the effects of crystallographic heterogeneity on adsorption are evaluated using computational molecular models. These results are then used to produce a more robust thermodynamic description of adsorption at the mineral-water interface.

A model describing the interactions of ferric iron with oxide ions, hydroxide ions, and water was developed and parametrized using a combination of empirical and theoretical information on Fe-OH potential energy surfaces. The model was constructed to describe as accurately as possible Fe-O, Fe-OH, Fe-OH₂, OH-H₂O, and H₂O-H₂O interactions in gas and condensed phases. The model also needed to be simple enough for use in large-scale calculations involving up to thousands of atoms in fully optimized positions and in molecular dynamics calculations. The model was tested by predicting the bulk structures of goethite, akaganeite, lepidocrocite, hematite, proton-ordered ice, gas-phase water clusters, the proton affinities of water and hydroxide ion, and structure and acidity of solvated Fe(H₂O)₆. The model was then applied to goethite (100), (010), (001), (110), and (021) surfaces using infinite slabs parallel to these crystallographic directions. This required extending existing methods for calculating forces and energies for infinite slabs with long-range forces to deal with our more complicated potential model.

Using the newly developed codes, structures and energies were computed for each plausible pattern of protons on neutral and fully hydroxylated slabs representing each of the five surfaces investigated. The lowest-energy protonation scheme for each of these neutral surfaces was identified.

Gas-phase proton affinities and acidities were computed by creating proton vacancies and interstitials at various sites on the slabs. To relate these energies to stability constants for surface protonation reactions, energies were computed for hydrolyzed ferric iron species in solution for which stability constants are known. The stability constants showed a very good linear relationship with the energies of the complexes as computed using the Fe-O-H model. This relationship was applied to compute equilibrium constants for proton equilibria on surface hydroxide and aqua sites. The surface stability constants were incorporated into a thermodynamic speciation code to calculate the extent of proton adsorption as a function of pH. The results were compared to experimental data. Using the unmodified relationship, the predicted point of zero charge was too low by approximately one log unit. The shape of the calculated curve was quite close to that of the experimental curve, however. If differential solvation between the surface and aqueous complexes is allowed to change to fit the point of zero charge, the titration data are well reproduced. A most interesting result is that the stability constants involving protonation/deprotonation of surface Fe₃OH, Fe₂OH, and FeOH groups are all very similar. The lack of variability was interrupted by the (010) surface, which has a particularly acidic site partially buried in the solid.

Publications

J.R. Rustad, A.R. Felmy, and B.P. Hay. "Molecular Simulation of Iron Oxide and Oxyhydroxide Minerals." *Geochim. et Cosmochim. Acta*. (submitted).

J.R. Rustad, A.R. Felmy, B.P. Hay, and J.W. Halley. "Molecular Statics Calculation of Proton Binding to Goethite Surfaces: A New Approach to Estimation of Stability Constants for Multisite Surface Complexation Models." *Geochim. et Cosmochim. Acta*. (submitted).

J.R. Rustad and J.W. Halley. "Ewald Methods for Polarizable Surfaces with Application to the Solvation of the (110) surface of α -FeOOH." *Journal of Chemical Physics* (submitted).

J.R. Rustad, B.P. Hay, and J.W. Halley. 1994. "Molecular Dynamics Simulation of Iron(III) and Its Hydrolysis Products in Aqueous Solution." *Journal of Chemical Physics*, 102, 427-431.

Relation Between $\log K$ of aqueous hydrolysis reaction
for $\text{Fe}(\text{OH})$, $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Fe}(\text{OH})_4$ and Gas-Phase

ΔE as calculated from model ($\log K = 0.027 * \Delta E$
(kcal/mol)).

(a)

Structure of the (001) surface
 of goethite. Unit cell is outlined
 in black, bond lengths are given
 in picometers

J. R. Rustad, A. R. Felmy, and B. P. Hay Pacific Northwest Laboratory

Surface Structure and Chemistry of Carbonate Minerals: Calcite Dissolution

Principal Investigators: D.R. Baer, J.P. LaFemina, and J.E. Amonette

Funding Source: Office of Basic Energy Sciences, Geosciences (KC-04-03-02)

Scientists at the Pacific Northwest Laboratory have been involved in an interdisciplinary theoretical and experimental effort to gain a fundamental, molecular level understanding of carbonate mineral surface structure and chemistry. In particular, atomic force microscopy (AFM) has been used to examine the calcite (10-14) cleavage surface and its dissolution behavior under a variety of solution conditions. Moreover, through the use of first principles quantum-mechanical and kinetic Monte Carlo calculations, we have constructed microscopic models capable of explaining the macroscopic dissolution behavior of this surface.

Carbonate minerals are particularly important in the global CO₂ cycle and in subsurface contaminant migration processes. By linking experimental and computational studies on well-defined surfaces, the factors controlling carbonate surface chemistry can be identified. In particular, the effects of substitutional impurities and other point defects on the structure and reactivity of carbonate surfaces and interfaces can be isolated and quantified, leading to new insights into the behavior of these materials in natural systems.

Atomic force microscopy has been used to examine the surface structure of CaCO₃ (10-14) surface in different aqueous solutions with atomic resolution. From these images, it appears that the cleaved calcite (10-14) surface exhibits a relaxed (1x1) structure in which the carbonate group within the surface unit cell reorients itself. Ab initio density-functional computations and glancing incidence x-ray diffraction measurements of this surface are being performed to determine if this relaxation is inherent to the calcite surface or is induced by the aqueous solution.

Dissolution on the (10-14) surface has been found to proceed via the formation of shallow pits. These pits are typically one atomic layer deep and pit growth is anisotropic as a result of differing atomic configurations at the pit step edges. The dissolution step velocities measured by AFM are 3.5 nm/s and 1.4 nm/s for the fast and slow directions, respectively. Measurements of the pit size dependence on temperature yield effective dissolution activation energies for the fast and slow directions of 0.61 eV and 0.64 eV. Other interesting features of these pits include the fact that the pit velocity is constant over

time; that the pits maintain their crystallographic shape, with straight edges, over time; and that the presence of impurities in the aqueous solution can significantly alter the surface morphology during dissolution.

Two models have been examined in an attempt to understand the microscopic factors controlling dissolution. The first is the analytical "terrace-ledge-kink" (TLK) model that relates the velocities of pit edge retreat to the frequency of "double-kink" and "kink" site formation. In this model, many different pit morphologies are possible depending upon the relative magnitudes of the double-kink and kink site formation frequencies. As a result, it is easily shown that crystallographically shaped pits with straight edges *and* a constant velocity retreat require a delicate balance in the frequency of double-kink and kink site formation (the "double-kink annihilation regime"). This model also indicates that the constant velocity phenomena is exhibited only after the pits reach a size that is significantly greater than the size of the fundamental atomic building blocks of the surface. Steps on pits smaller than this accelerate as they retreat. This prediction has not yet been verified experimentally because of the difficulty of imaging nanoscale pits with the AFM.

To investigate dissolution quantitatively, we have constructed a simple, two-parameter, kinetic Monte Carlo (KMC) model in which the activation energy for the removal of a surface species is based upon its near-neighbor coordination. Using this model we have been able to reproduce all of the available experimental data, including the temperature dependence of pit size and the evolution of pit size as a function of time. The model also reproduces the acceleration regime for small pits predicted by the TLK model, as well as the transition to a constant velocity regime for pits significantly larger than the atomic dimensions of the surface. Finally, from this model we have derived the fundamental microscopic rates for the elementary pit dissolution surface processes.

Future work in this area will focus on the effects of impurities on the dissolution mechanism and rate. In particular, the role of impurity defects in controlling the surface morphology during dissolution will be investigated via high-resolution experimental studies of the defected surfaces, combined with first-principles and

kinetic Monte Carlo studies to elucidate the microscopic mechanisms controlling the defect-mediated dissolution.

Publications

Y. Liang, D.R. Baer, and A.S. Lea. "Dissolution of CaCO_3 (10-14) Surface." In *Proceedings of the 1994 Materials Research Society*.

Y. Liang, A.S. Lea, D.R. Baer, and M.H. Englehard. "Structure of the Cleaved CaCO_3 (10-14) Surface in Aqueous Environment." *Surf. Sci.* (submitted).

A.J. Skinner, J.P. LaFemina, and H.F. Jansen. 1994. "Structure and Bonding in Calcite CaCO_3 : A Theoretical Study." *Am. Mineralogist* 79, 205.

An eccentric, deep pit showing the anisotropic dissolution behavior of the calcite surface

The linear increase in pit size with time showing a constant step velocity during the pit growth

Results of KMC Computations

- Accelerating steps for small pits
- Transition to constant velocity
- Excellent agreement with AFM data

Pit size (in lattice units [LU]) vs. time (seconds) comparison of the experimental AFM data (line) and results of KMC computations (symbols). Figure at left shows the entire time range for which experimental data exists. The figure on the right shows the first 160 seconds.

Environmental Molecular Sciences Laboratory

Rates of Elementary KMC Events at 300 K

Three-fold coordinated sites:

■ *slow* = 0.014 s^{-1}

■ *fast* = 0.117 s^{-1}

Two-fold coordinated sites:

■ *slow-slow* = 63 s^{-1}

■ *slow-fast* = 528 s^{-1}

■ *fast-fast* = 4414 s^{-1}

Pacific Northwest Laboratory

A schematic illustration of the rates of elementary dissolution events (at 300K) computed from the kinetic Monte Carlo model. As is evident from the illustration, the rates are highly dependent upon the near-neighbor coordination and vary greatly with orientation in either the fast or slow directions.

KC-07 Applied Mathematics

High Performance Scientific Computing Using Global Arrays

Principal Investigators: J. Nieplocha, R.J. Harrison, and R.J. Littlefield

Funding Source: High Performance Computing and Communications Program of the Office of Computational and Technology Research, Mathematical, Information and Computational Sciences Division (KC-07)

The Global Arrays are a new parallel programming environment for development of scientific application on massively parallel computers. The key concept of Global Arrays is that it provides a portable interface through which each process in a multiple instruction, multiple data parallel program can efficiently access logical blocks of physically distributed matrices, with no need for explicit cooperation by other processes (or processors) where the data resides.

This work addresses the issue of how to program large scalable scientific applications. For a range of applications, the Global Arrays model provides a better combination of simple coding, high efficiency, and portability than are provided by other models. For example, the Global Arrays model provides good support for a large part of computational chemistry, especially electronic structure codes, and it shows promise for application domains like global climate modeling, where application codes often exhibit both spatial locality and load imbalance.

The Global Arrays model and tools were developed under a DOE HPCCI Grand Challenge project in High Performance Computational Chemistry, whose focus is on developing algorithms, techniques, and tools for allowing computational chemistry applications to exploit future teraflops machines. However, the Global Arrays model

and tools have immediate benefit, and are now being widely adopted in parallel chemistry codes in the Pacific Northwest Laboratory's Environmental Molecular Sciences Laboratory and elsewhere. Such rapid adoption of a new programming strategy illustrates the power of the HPCCI program in bringing together an effective collaboration of researchers from computer science and the application domains.

The Global Arrays is a public domain toolkit supported on a wide range of distributed and shared memory computer systems including

- Distributed-memory, message-passing parallel computers with interrupt-driven communications or Active Messages (Intel iPSC/860, Delta and Paragon, IBM SP-1/2)
- Networks of uni- and multi-processor Unix workstations
- Shared-memory parallel computers (KSR-1/2, Cray T3D, SGI).

The Global Arrays toolkit is available on an anonymous ftp server <ftp.pnl.gov> in directory `pub/global`. Further information is provided on WWW at <http://www.emsl.pnl.gov:2080/docs/global/ga.html>.

KP-01 Analytical Technologies

Advanced Capillary Electrophoresis-Mass Spectrometric Methods for Biopolymer Characterization

Principal Investigators: R.D. Smith, S.A. Hofstadler, and H.R. Udseth

Funding Source: Office of Health and Environmental Research, Measurement Science Program (KP-01-02-00)

Significant advances in biological and medical research would be derived from the ability to identify proteins and their modifications that are expressed at low levels or where the cellular population is limited. Similarly, one of the greatest bioanalytical challenges is to be able to provide detailed chemical information from single biological cells for investigation of perturbed cellular processes that would be precluded by statistical limitations that necessarily exist for large cell populations. At present, only very limited capabilities exist for single-cell analysis due to the significant analytical demands; sample volumes of < 100 femtoliters and sensitivities for detection at the attomole (10^{-18} moles) and zeptomole (10^{-21}) levels, and even lower. Although mass spectrometry has become widely recognized as one of the most informative methods for protein characterization, previous work fell far short of the sensitivity needed and proved inadequate for dealing with the complexity of the cellular milieu. A series of developments at Pacific Northwest Laboratory has now made possible such applications.

These recent developments include the use of capillary electrophoresis (CE) with electrospray ionization and high resolution multistage Fourier transform ion cyclotron resonance mass spectrometry (ESI-FTICR). CE methods provide a basis for separating cellular constituents and reducing the complexity of the components presented to the ESI-FTICR at any point. The complexity and wide range of protein concentrations in cells required that a new approach be developed to provide the necessary dynamic range. A novel approach for recording major components in the mass spectra, and then automatically removing them to "fill" the FTICR ion trap with lower abundance species has been developed based upon the use of "colored noise" quadrupole excitation waveforms. This approach has led to a three-order-of-magnitude improvement in the effective dynamic range of ESI-FTICR studies and has enabled preliminary experiments at the single-cell level.

In initial studies, erythrocytes (red blood cells) have been used and single-cell sensitivity has been demonstrated for selected cell components. Importantly, using the multistage capabilities of FTICR, detailed information on the amino acid sequences and sites of modifications can be

obtained. This initial demonstration was for the most abundant protein (hemoglobin), but the results clearly indicate that further refinement of methods and the implementation of the advanced 12-tesla FTICR instrumentation under development for the EMSL, will allow progression to low-level components. New approaches based upon the previously established ability to analyze single molecular ions also promise to greatly extend these capabilities. One possible application of these methods is to rapidly identify microorganisms through the characterization of proteins, membrane phospholipids, or other cellular components. This key capability would also provide opportunities for research at the cellular level, including individual cells subjected to various radiation or chemical insults. Perhaps most important will be applications with larger cell populations involving the identification of unknown proteins, using protein or genomic databases that are correlated with disease states and for which present methods are often inadequate.

Publications

J.E. Bruce, G.A. Anderson, and R.D. Smith. "Colored Noise Waveforms and Quadrupole Excitation for Dynamic Range Expansion in Fourier Transform Ion Cyclotron Resonance Mass Spectrometry." *Anal. Chem.* (submitted).

S.A. Hofstadler, F.D. Swanek, D.C. Gale, A.G. Ewing, and R.D. Smith. 1995. "Capillary Electrophoresis-Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry for the Direct Analysis of Cellular Proteins." *Anal. Chem.* 67, 1477-1480.

S.A. Hofstadler, J.H. Wahl, R. Bakhtiar, G.A. Anderson, J.E. Bruce, and R.D. Smith. 1994. "Capillary Electrophoresis Fourier Transform Ion Cyclotron Resonance Mass Spectrometry with Sustained Off-Resonance Irradiation for the Characterization of Protein and Peptide Mixtures." *J. Amer. Soc. Mass Spectrom.* 5, 894-899.

D.W. Mitchell and R.D. Smith. "The Cyclotron Motion of Two Coulombically Interacting Ion Clouds with Implications to Fourier Transform Ion Cyclotron Resonance Mass Spectrometry." *Phys. Rev. E* (in press).

D.C. Muddiman, A.L. Rockwood, Q. Gao, J.C. Severs, H.R. Udseth, R.D. Smith, and A. Proctor. "Application of Sequential Paired Covariance to Capillary Electrophoresis Electrospray Ionization Time-of-Flight Mass Spectrometry; Unraveling the Signal from the Noise in the Electropherogram." *Anal. Chem.* (submitted).

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Z. Zhao, J.H. Wahl, H.R. Udseth, S.A. Hofstadler, A.F. Fuciarelli, and R.D. Smith. 1995. "On-line Capillary Electrophoresis-Electrospray Ionization Mass Spectrometry of Nucleotides." *Electrophoresis* 16, 389-395.

Direct Cellular Analysis

Demonstration of the direct analysis of a protein (hemoglobin) from red blood cells. One or more red blood cells are directly sampled and are then lysed and separated by capillary electrophoresis a) high resolution mass spectra are obtained using FTICR, as shown for the alpha chain of hemoglobin b) a specific species can then be isolated and effectively dissociated c) from which the high resolution obtained for the fragments d) provides extensive information on the sequence and the sites of modifications.

KP-02 Environmental Research

Aircraft Observations of Atmospheric Gravity Waves and Their Influence on Local Ozone Concentrations

Principal Investigators: X. Bian, C. Berkowitz, and S. Zhong

Funding Source: Office of Health and Environmental Research, Atmospheric Chemistry Program (KP-02-01)

Ozone is an airborne chemical linked not only to health effects, but to many photochemical processes and climate dynamics. Aircraft measurements of ozone and related trace gases were made over the western North Atlantic Ocean by the Department of Energy's Gulfstream-1 aircraft during the summer of 1992 to quantify the fate of these species. One objective of the program was to improve our understanding of the distribution of natural ozone. This highlight illustrates one component of the distribution of natural ozone.

A wave-like pattern in moisture, temperature, and ozone were observed while sampling at a constant elevation during several aircraft missions flown under conditions of strong atmospheric stability. The top- and bottom-left sides of the accompanying figure show a representative wave pattern having a minimum in the measured dew point associated with an ozone maximum. This pattern was observed only for trace gases having a well-defined vertical gradient (e.g., ozone, moisture, and temperature). Trace species not exhibiting a vertical gradient did not exhibit this pattern, nor did trace gases associated with human activity (sulfur dioxide, carbon monoxide). We postulate that the aircraft flew through the undulating interface between the surface boundary layer (lower ozone concentrations) and the free troposphere (higher

ozone concentrations). We further postulate that these undulations were caused by an internal gravity wave that was propagating along that interface.

To test these hypotheses, we developed a numerical model that combined an analytic solution for gravity waves with the advection-diffusion equation. Initial conditions for the model were based on observations of ozone in the boundary layer (40 ppb) and aloft (80 ppb). A horizontal wavelength of 200 kilometers and a vertical scale of 2 kilometers were assumed based upon harmonic analysis of the ozone and temperature observations. The top-right panel shows the vertical distribution of ozone 1.5 hour into the simulation and illustrates in the bottom-right panel what an aircraft flying at 1.7 kilometers MSL would sample. The similarity between the observed and modeled ozone time series strongly supports our hypothesis that the G-1 measured ozone and dew point temperature in an internal gravity wave.

Publication

X. Bian, C.M. Berkowitz, and S. Zhong. "Aircraft Observations of Possible Gravity Waves and Associated Ozone Maximum." To appear in Preprints, 1995 Fall AGU Meeting, San Francisco, California, American Geophysical Union.

Aircraft Observations of Atmospheric Gravity Waves and Their Influence on Local Ozone Concentrations

aircraft observation

conceptual model

Principal Investigators: Xindi Bian, Carl Berkowitz and Shiyuan Zhong
Funding Source: DOE OHER Atmospheric Chemistry Program

Pacific Northwest Laboratory

Boundary-Layer Processes and the Formation of Ozone Profiles over the Western North Atlantic

Principal Investigators: J.C. Doran, S. Zhong, C. M. Berkowitz

Funding Source: Office of Health and Environmental Research, Atmospheric Chemistry Program (KP-02) and Atmospheric Studies in Complex Terrain

Vertical profiles of ozone, $\text{NO} + \text{NO}_2$, and other by-products of industrial activity have long been the primary means used to describe chemistry in the lower troposphere. The magnitude and shapes of these profiles have been used to infer processes related to the species of interest.

The explanation of many characteristic trace gas profiles are based only on photochemical arguments. Here we consider the role of boundary-layer mixing on profiles of ozone measured by the Department of Energy's Research Aircraft Facility during the Pacific Northwest Laboratory's participation in the North Atlantic Regional Experiment (NARE) of 1992. We now believe that elevated ozone mixing ratios found aloft are natural in origin, and that boundary-layer mixing, in addition to photochemical mechanisms, may play an important role in the formation of such profiles.

On several days, a well-mixed boundary layer was observed in conjunction with ozone mixing ratios < 25 to 35 ppb. Ozone above this well-mixed layer abruptly increased to ≈ 50 ppb. Earlier work suggested that surface removal through dry deposition had depleted surface ozone. Our recent work suggests that large-scale vertical motions may play an equally important role in defining these profiles.

Our investigation used a three-dimensional mesoscale model having a prognostic equation for turbulence kinetic energy and a surface energy exchange module for calculating surface sensible and latent heat fluxes to the atmosphere. A Lagrangian particle dispersion model was used to track the trajectories of air parcels and to estimate their horizontal and vertical diffusion. Particle concentration was used as a surrogate for ozone mixing ratio. The mesoscale model was initialized with meteorological observations from the National Meteorological Center.

A large number of particles were released at a rate that increased linearly with height from a source region previously identified by isobaric back-trajectories. We found that while turbulent mixing within the boundary layer produced a uniform value within the lowest 1.5 kilometers of the atmosphere, the particles encountered a series of up- and down-draft regions during their transport to the Western North Atlantic (WNA) and these vertical motions gave rise to a nearly uniform distribution of particles in the low portion of free troposphere above the boundary layer. These model simulations are consistent with the 1992 aircraft observations over the WNA. Mixing processes alone (no chemical processes) could explain the shape of the observed ozone profiles.

Boundary-layer circulations thus appear to play an important role in the development of ozone profiles showing a jump-discontinuity at the top of the mixed layer. Future work will add an explicit photochemical description to these results to further examine this relation between mesoscale meteorology and tropospheric chemistry.

Publications

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Boundary-Layer Processes and the Formation of Anomalous Ozone Profiles over the Western North Atlantic

DNAPL Flow in Heterogeneous Geologic Media

Principal Investigators: M. Oostrom and M.D. White

Funding Source: Office of Health and Environmental Research, Subsurface Science Program (KP-02-03), and Office of Environmental Management, Office of Technology Development

The subsurface environment below many Department of Energy sites is contaminated with organic liquids, including DNAPLs (dense non-aqueous phase liquids) such as trichloroethylene (TCE), perchloroethylene (PCE), and carbon tetrachloride. These contaminants are immiscible with water and migrate as separate phases whose behavior is very difficult to predict and for which effective cleanup methods do not exist.

Geoscientists and modelers in the OHER Subsurface Science Program are conducting basic research that applies to problems faced by the DOE Office of Environmental Management in its cleanup efforts. The research focuses on developing a fundamental understanding of DNAPL behavior by coupling theoretical investigations with intermediate-scale experimentation in PNL's Subsurface Environmental Research Facility (SERF). Research has focused on understanding how physical, chemical, and microbiological conditions in the subsurface control interaction of water and DNAPL and dictate conditions under which they are retained in porous media or transported as separate phases. For example, density-driven vapor flow has been demonstrated at the intermediate scale to be an important mechanism for DNAPL dispersion in the unsaturated zone while preferential flow in saturated media has been shown to be dependent on specific fundamental physical processes.

Recent laboratory investigations of DNAPL infiltration into a variety of porous media have demonstrated the grossly nonhomogeneous flow behavior of DNAPL across porous media interfaces and saturation boundaries. The fundamental information acquired from these basic investigations is now being used to solve site-specific contamination problems, such as at DOE's Paducah Gaseous

Diffusion Plant in Kentucky, where TCE is a major contaminant. Unfortunately, little is known about the flow and retention behavior of DNAPL in the heterogeneous soil layers beneath the Paducah site or other layered systems across the DOE complex. Development and implementation of sound remediation strategies at the Paducah site includes applying scientific knowledge of DNAPL flow patterns across porous media interfaces in order to arrive at an accurate description of the flow patterns at the site.

Publications

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R.J. Lenhard, M. Oostrom, and M.D. White. "Modeling Fluid Flow and Transport in Variably Saturated Porous Media with the STOMP Simulator; 2. Verification and Validation Exercises." *Advances in Water Resources* (in press).

M. Oostrom, J.H. Dane, B.C. Missildine, and R.J. Lenhard. 1995. "Error Analysis of Dual-Energy Gamma Radiation Measurements." *Soil Science* 160(1):28-42.

M.D. White, M. Oostrom, and R.J. Lenhard. "Modeling Fluid Flow and Transport in Variably Saturated Porous Media with the STOMP Simulator; 1. Nonvolatile Three-Phase Model Description." *Advances in Water Resources* (in press).

Intermediate-scale soil column showing the complex pattern of vertical and horizontal DNAPL movement in a relatively homogeneous saturated sand column. Research performed at the Pacific Northwest Laboratory

Forecasting Sudden Wind Shifts over the Hanford Site

Principal Investigators: J.C. Doran and S. Zhong

Funding Source: Office of Health and Environmental Research, Environmental Sciences Division (KP-02-01-00-0)

A peculiar and characteristic feature of the local meteorology at the Hanford Meteorology Station (HMS) during the late spring and summer is the rapid development of moderately strong winds (7 to 10 m/s or more) from the northwest around sunset. These winds, called "regional drainage winds," typically persist for about 6 hours and then weaken. Despite their strength, the winds often have a local aspect to them—at some sites 30 to 40 kilometers farther to the east, they are sometimes weaker or not observed at all. Forecasters at the Station have long known that the occurrence of these winds is strongly correlated with the magnitude of the midday temperature difference between HMS (~220 meters MSL) and locations near the crest (~2000 meters MSL) of the Cascade Range; the larger the difference, the stronger the winds. If the temperature difference is less than approximately 10 K, the winds are unlikely to develop at all. Forecasters also suggested that the timing of the onset of these flows may be linked to the direction of the synoptic-scale wind, with winds from the southwest resulting in later onset times than those from the west or northwest. Because these winds are such a common feature, an improved understanding of their origin, sensitivity to larger-scale meteorological conditions, and the strength and timing of their occurrence has a number of potential practical forecasting uses, such as during periods of significant fire danger over the Hanford Site when shifts in wind speed and direction can be critically important.

An analysis of these winds was conducted at Pacific Northwest Laboratory by scientists in the Department of Energy's Atmospheric Studies in Complex Terrain (ASCOT) Program using data taken from two principal sources, the 15-meter wind speed and direction data obtained at the HMS and measurements obtained from

the Public Agriculture Weather System (PAWS), a network of surface meteorological observation stations operated by Washington State University. In addition, a numerical mesoscale model was used to conduct a set of simulations to determine the causes of the regional drainage winds and to study their dependence on synoptic weather conditions. The study revealed the following features. As heating of the surface proceeds during the day, a temperature gradient develops over the state with cooler air to the west and warmer air to the east. Winds with a westerly component gradually move eastward but by mid-afternoon are still confined to a region near and just to the east of the Cascade Crest. Upslope winds driven by heating of the eastern slopes of the Cascades help block further advances of cooler westerly winds during the mid-afternoon period of strong heating. In the early evening, as the surface heating decreases, these upslope winds die away and the cooler air mass moves more rapidly to the east. Winds generated by local cooling may contribute at this time, further enhancing the strength and eastward propagation of the cool air mass. The depth of the flows at HMS can reach ~1000 meters or more. In the Kittitas Valley region east of Snoqualmie Pass, terrain channeling imposes a northwest direction on the air flow. In regions farther to the east and south, the Coriolis force plays a similar role, diverting the eastward-moving winds toward the south, and producing a general flow from the northwest over the whole region to the east of the higher terrain.

Publication

J.C. Doran and S. Zhong. 1994. "Regional Drainage Flows in the Pacific Northwest." *Mon. Wea. Rev.*, 122, 1158-1167.

t = 1800 LT

20 km
14 m/s
←

Simulated Wind Fields Over Southcentral Washington Showing Strong Discontinuity in Wind Speed and Direction as Regional Drainage Winds Approach the Hanford Site (HMS = Hanford Meteorological Station; E = Ellensburg)

S9305099.2a

Hydrogen-Driven Subsurface Ecosystems May Be a Significant New Energy Source

Principal Investigators: T.O. Stevens and J.P. McKinley

Funding Source: Office of Health and Environmental Research, Subsurface Science Program (KP-02-03)

As a result of investigations of deep microbial communities at the Hanford Site, an OHER Subsurface Science Program research team at Pacific Northwest Laboratory discovered a geochemical source of hydrogen gas from room temperature reactions between water and rocks. A subsequent extended survey of confined aquifers in the region showed that H_2 -utilizing microorganisms outnumbered organisms using organic-matter by several orders of magnitude. Thus, H_2 may serve as a previously unrecognized source of chemical energy driving deep microbial ecosystems.

Scientists initially observed unusually high concentrations of hydrogen gas accumulating in the borehole. Subsequent laboratory investigations revealed that H_2 was produced by reactions between groundwater and the finely crushed basalt particles produced by the drilling operations. While hydrogen production from basalt weathering has been reported previously, it is usually assumed to require the high temperatures found in geothermal settings. This research demonstrates that H_2 can be produced by water-rock interactions under milder conditions. The scientists also showed that reduced iron plays a key role in H_2 production in the basalt.

The discovery led to new drilling safety procedures at Hanford to avoid the risks of explosive gas in boreholes. However, this discovery also has important new implications for microbial ecology in the deep subsurface and may provide clues for how life originated and functioned on Earth billions of years ago and for the possibility of

life on Mars or other planetary bodies. Such H_2 producing reactions could have been a source of life before photosynthesis and may provide a subsurface energy source that is independent of oxygen and organic matter produced by photosynthetic energy. Such a system may exist beneath the Hanford Site in aquifers confined with the Columbia River basalt flows at great depth.

The Columbia River basalts cover a 163,000 km² area in the northwestern United States to a depth of several kilometers, and similar formations are found around the world. As such, and based on preliminary hypotheses, these deposits may represent a massive new source of chemical energy, probably in the form of reduced iron. As water slowly percolates through these formations, the energy is released and made available to deep subsurface microbial ecosystems.

Publications

B.M. Bjornstad, J.P. McKinley, T.O. Stevens, S.A. Rawson, J.K. Fredrickson, and P.E. Long. 1994. "Generation of Hydrogen Gas as a Result of Percussion Drilling Within an Unconfined Aquifer, South-Central Washington." *Groundwater Monitoring and Remediation* 14:140-147.

T.O. Stevens, and J.P. McKinley. "Lithoautotrophic Microbial Ecosystems in Deep Basalt Aquifers." *Science* (in press)

Confocal laser micrograph showing bacterial biofilm community in a deep basalt aquifer. The bacteria, shown in red, derive energy for growth and metabolism from geochemically produced hydrogen. Research performed at the Pacific Northwest Laboratory.

The Influence of Regional-Scale Atmospheric Circulations on Chemical Mixing over the Western North Atlantic

Principal Investigators: J.D. Fast and C.M. Berkowitz

Funding Source: Office of Health and Environmental Research, Atmospheric Chemistry Program, and Atmospheric Studies in Complex Terrain Program (KP-02-01-00-0)

The east coast of the United States is a major source of pollutants for the airshed of the Western North Atlantic (WNA). Ozone is an export pollutant of key interest because of its role in initiating many photochemical processes and because of its role in climate dynamics as a greenhouse gas. The Department of Energy's Atmospheric Chemistry Program participated in an international study to evaluate the outflow of ozone and other pollutants into the WNA during the summer of 1993. The work presented here highlights results from a joint study by the Atmospheric Chemistry Program (ACP) and the Atmospheric Studies in Complex Terrain (ASCOT) to more clearly understand atmospheric circulation patterns associated with observed chemical features.

An atmospheric mesoscale model and a Lagrangian particle dispersion model were used to investigate the relationship between boundary-layer processes, mesoscale circulations, and the airborne measurements of ozone taken over Yarmouth, Nova Scotia, in the summer 1993 field campaign. Preliminary results of this analysis have shown that eastward moving plumes from North America cannot be characterized by a unique age, but that mixing from a variety of source regions results in a spectrum of ages; this result at least partially explains known ambiguities in previous estimates of plume age based on the ratios of measured hydrocarbon concentrations. Vertical profiles of particle concentrations were similar in shape to profiles of ozone, suggesting that the mesoscale and local circulation patterns were being correctly modeled.

The accompanying figure illustrates model results for two case studies. As shown in the lower panel ("path of elevated plume") much of the mixing appeared to be due to convective processes over land lofting urban material into the free troposphere followed by transport within cyclonic synoptic circulations. As a consequence of the complexity

of these circulation patterns, plume age was found to not be a good measure of transport distance and therefore not a good indicator source region. These particles remained aloft as they were advected above the cool stable layer consistent with earlier calculations suggesting that export from the boundary layer contributes a significant amount of the total ozone export from the United States to the free troposphere.

The upper panel illustrates a second scenario of ozone transport into the WNA. In this case, observations made near the surface of the oceans had relatively local continental source regions as a consequence of weak surface winds. These light winds slowly transport material within a shallow stable layer toward Yarmouth ("stable layer adjacent to ocean surface").

In the future, the Pacific Northwest Laboratory's Global Chemistry Model will be coupled to the atmospheric mesoscale fields to further examine the mechanisms controlling the layering of ozone in the vicinity of Nova Scotia.

Publications

C.M. Berkowitz and J.D. Fast. "The Influence of Regional-Scale Atmospheric Circulations on Chemical Mixing over the Western North Atlantic." To appear in Preprints, Ninth Joint Conference on the Applications of Air Pollution Meteorology with the AWMA. Atlanta, Georgia, American Meteorological Society.

J.D. Fast and C.M. Berkowitz. "Comparison of Forward and Back Trajectories with Ozone Transport over the Western North Atlantic." To appear in Preprints, 1995 Fall AGU Meeting, San Francisco, California, American Geophysical Union.

Dispersion Simulations during the 1993 North Atlantic Regional Experiment (NARE)

Near-Surface Plume over Nova Scotia

Elevated Plume over Nova Scotia

Pacific Northwest Laboratory

In Situ Redox Manipulation to Control Mobility of Toxic Metals

Principal Investigator: J.S. Fruchter

Funding Source: Office of Health and Environmental Research, Subsurface Science Program (KP-02-03), and Office of Environmental Management, Office of Technology Development

The mobility of toxic and hazardous metals and radionuclides in the subsurface is often governed by their oxidation (redox) state. Fundamental research by Pacific Northwest Laboratory scientists in the OHER Subsurface Science Program led to the development of a novel concept for control of metal and radionuclide behavior by manipulating the subsurface redox potential. The concept has been transferred to DOE, Environmental Management, for implementation in cleanup at the Hanford Site. The concept makes use of the complex natural interactions between subsurface minerals and groundwaters. Both innocuous chemical injection and indigenous microorganisms may be used to advantage in using these interactions to retard contaminant movement.

The overall objective of the project is to test the interaction of chemical reagents and microbiological nutrients with the natural subsurface system and to understand the long-term effectiveness of these treatments in controlling the geochemistry of subsurface water systems. Because of the complexity of subsurface systems, these interactions are not easily investigated or simulated in the laboratory. The approach is to conduct single-well, forced-gradient, reactive tracer experiments in shallow unconfined aquifers that are representative of groundwater environments requiring restoration. The advantages of this method include well-defined initial conditions, the ability to restrict the movement of solutes to specific zones in the aquifer, and the fact that minimal volumes of subsurface materials are required for characterization. Reagents designed to temporarily decrease the redox potential of the aquifer will be injected, and their effects on both the aquifer and solid phases will be assessed through sampling wells and core samples.

Basic research results led to the selection of sodium dithionate as the first reagent to be studied in the field. Dithionate was shown in the laboratory to be capable of reducing solid phase iron, in turn reducing mobile

chromate to immobile chromium hydroxide and iron chromium hydroxide. A field experiment to test the feasibility of the concept is under way, with the full experiment scheduled for FY 1996 and FY 1997. The full experiment was recently incorporated into the Hanford Site Five-Year Plan as a field treatability study of the 100 D Area chromate plume, an Operable Unit under CERCLA. The experiment will entail dithionite injection to reduce sediment ferric to ferrous iron thus creating a permeable subsurface barrier approximately 200 feet long. Mobile chromate passing through the barrier will be reduced by the ferrous iron to highly immobile chromium hydroxide or iron chromium hydroxide forms that no longer pose a threat to human health or the environment. The work scope has been reviewed and accepted by Bechtel-Hanford Company, the site environmental restoration contractor, by DOE-EM (EM-40), and by Washington State and Environmental Protection Agency regulators. If successful, this will be a replacement technology for the current best available pump and treat technology.

Publications

J.S. Fruchter, F.A. Spane, J.K. Fredrickson, C.R. Cole, J.E. Amonette, J.C. Templeton, T.O. Stevens, D.J. Holford, L.E. Eary, B.N. Bjornstad, G.D. Black, J.M. Zachara and V.R. Vermeul. 1994. *Manipulation of Natural Subsurface Processes: Field Research and Validation*. Final report. Subsurface Science Program, Office of Health and Environmental Research and the In Situ Remediation Technology Development Integrated Program, Office of Technology Development, U.S. Department of Energy, Washington, D.C. PNL-10123/UC-402,802.

Y.A. Gorby, D.W. Kennedy, and J.E. Amonette. 1994. "Reduction of Structural Iron in Layered Silicates by Dissimilatory Fe(III)-Reducing Bacteria." In *Proceedings of the American Society of Microbiology*.

In Situ Permeable Treatment Barrier

84303023.1

- * Potential Candidate for Redox Treatment
- ** Favorable Candidate for Redox Treatment

Conceptual approach to the creation of a chemical subsurface treatment barrier for reducing the mobility of metals and radionuclides. Research performed at the Pacific Northwest Laboratory.

Molecular Probes for Bioremediation Monitoring

Principal Investigator: F.J. Brockman

Funding Source: Office of Health and Environmental Research, Subsurface Science Program (KP-02-03) and Environmental Management, Office of Technology Development

Researchers from Pacific Northwest Laboratory, the Idaho National Engineering Laboratory, and Montana State University have applied concepts for monitoring biological activity that were developed in the Subsurface Science Program to the bioremediation of Hanford groundwater contaminated with nitrate and carbon tetrachloride. Bioremediation is accomplished by adding acetate, a nontoxic carbon source, to the subsurface to stimulate indigenous microbial communities to utilize all of the oxygen that is present. Once conditions become anaerobic, the microorganisms use nitrate in place of oxygen and fortuitously degrade carbon tetrachloride by a process known as co-metabolism.

In the past, monitoring bioremediation activity has relied on indirect methods, such as counting the number of bacterial colonies that appear on an agar plate following dilution of a groundwater or subsurface sediment sample and correlating that number with measurements of the disappearance of contaminants of interest or terminal electron acceptors, such as oxygen or nitrate. This method does not, however, directly estimate biomass or activity of the bacteria responsible for biodegradation and

cannot be used to distinguish among other phenomena, such as advection/dispersion or surface adsorption of contaminants, or for enhancing system performance. These limitations are overcome by using molecular probes that are designed to detect the presence and abundance of ribosomal RNA (rRNA) synthesized by microorganisms for the production of specific proteins, such as the enzymes directly responsible for contaminant destruction. The molecular probes recognize and bind to the rRNA of interest both specifically and quantitatively and are currently being tested at Hanford in conjunction with novel in-well sampling devices that permit the measurements to occur in real time. In addition to providing significantly more useful information, this method reduces the time and cost involved in obtaining and analyzing samples.

Publication

A. Ogram, W. Sun, F.J. Brockman, and J.K. Fredrickson. 1995. "Isolation and Characterization of RNA from Low-Biomass Deep-Subsurface Sediment." *Applied and Environmental Microbiology* (61)763-768.

Verifying Biodegradation During Bioremediation

Ribosomal RNA (rRNA) is extracted from microorganisms collected on filters placed in groundwater wells. The rRNA is hybridized with RNA probes that have been designed to react specifically with rRNA from microorganisms that degrade the contaminant of interest giving a time and space-integrated monitoring profile of comparative activity during nutrient addition and groundwater recirculation phases of a bioremediation system

Pacific Northwest Laboratory

Nocturnal Boundary Layer Evolution Within a Canyonland Basin

Principal Investigators: J.D. Fast, C.D. Whiteman, and S. Zhong

Funding Source: Office of Health and Environmental Research, Atmospheric Studies in Complex Terrain Program (KP-02-01-00-0)

Many communities in the western United States are located within basins, magnifying the importance of being able to predict the transport and diffusion of hazardous materials in these areas. Observations and modeling studies have indicated that flows within basins can be affected by larger-scale ambient influences. These multiple-scale interactions can produce highly variable flow patterns, in space and in time, that complicate the prediction of atmospheric circulations and pollutant dispersion. Atmospheric models should provide valuable information about basin energetics since data sets obtained from numerical simulations represent dynamically balanced realizations of such flows.

An atmospheric mesoscale model was used in this study to examine the nocturnal boundary layer evolution within the Sinbad basin in western Colorado. The model results were compared to wind and temperature data collected during a field experiment in the summer of 1988. It was found that the model was able to reproduce the overall amount of cooling within the basin and the flow exiting the basin. Evaluation of the individual terms in the potential temperature equation showed that advection and diffusion terms were significantly larger along the side walls than within the basin, indicating that measurements made within the basin would not necessarily be representative of the basin as a whole. This further suggests that studies which use only a few point measurements in

a basin may significantly misrepresent the individual terms of the basin energy budget.

The wind and turbulence fields produced by the mesoscale model were also used by a Lagrangian particle dispersion model to determine the transport and diffusion of a tracer released along the side walls of the basin. The results indicated that flows within even simple basins, such as the Sinbad basin, can be quite complex in both space and time. For instance, eddies in the flow field formed and dissipated within the basin in a matter of hours. These eddies circulated the tracer around the basin floor before it exited through the canyon. Dispersion of the tracer revealed that pollutants released within the basin would remain trapped below the basin rim. The atmospheric and dispersion models used in this study will also be employed as part of the Department of Energy's Mexico City Air Quality Research Initiative (MARI) to determine how basin energetics affect air quality in the vicinity of Mexico City.

Publication

J.D. Fast, S. Zhong, and C.D. Whiteman. "Nocturnal Boundary Layer Evolution Within a Canyonland Basin." *Journal of Applied Meteorology* (to be submitted).

Nocturnal Dispersion within Sinbad Basin

**Pace Peak
(2750 m)**

**Salt Wash Canyon
(1572 m)**

- *mesoscale model results coupled to a Lagrangian particle dispersion model*
- *tracer released from 7 pm to 1 am LST*

Pacific Northwest Laboratory

Nocturnal Dispersion within Sinbad Basin

Pace Peak
(1572 m)

Sinbad Basin

Salt Wash Canyon
(1572 m)

- mesoscale model results coupled to a Lagrangian particle dispersion model
- tracer released from 7 pm to 1 am LST

Novel Drilling Method to Define Microbial Heterogeneity in Unconsolidated Vadose Zone Sediments

Principal Investigators: F.J. Brockman and C.J. Murray

Funding Source: Office of Health and Environmental Research, Subsurface Science Program (KP-02-03)

Scientists at Pacific Northwest Laboratory have teamed with industry to develop novel horizontal drilling methods to assess microbial distribution in unconsolidated heterogeneous sediments. The new methods are now being applied in research and site cleanup. Investigating the pattern of microbial distribution in subsurface environments is important, because subsurface microbial populations can have a large influence on contaminant transport and offer strong potential for in situ remediation. For these reasons, information on their spatial distribution is needed.

Research on spatial variability utilizes geostatistical methods that require the specialized acquisition and analysis of subsurface samples down to the centimeter scale. This level of sophistication is needed to quantitate microbial relationships with other geochemical and physical properties. Sampling the horizontal and vertical directions is required. Drilling and sampling techniques in the vertical direction are well established. However, horizontal sampling experience and data are limited. To meet these requirements, PNL scientists teamed with Tonto Drilling Sciences, Inc., to develop novel methods to collect representative core samples of the unconsolidated sediments in the horizontal direction of accessible outcrops. Standard methods that employ drilling fluids (e.g., air, water, mud) and a rotating core barrel could not be used, since those methods can contaminate the cores with microorganisms that are not representative of the sampled interval. Drilling also had to accommodate aseptic sample collection and handling methods developed by the OHER Subsurface Science Program, including the use of sterilized core liners and the use of tracers to identify core material contaminated by non-indigenous microbes.

The drilling method developed was a modified version of the hollow-stem-auger technique. Narrow auger strips were affixed to the outside of the drill rods to remove cuttings from around the outside of the drill rod and facilitate the advancement of the drill rods. Cores (0.5 meters long) were collected by driving the coring assembly ahead of the drill rods, then the drill rods were advanced by the auger method. The core assembly was advanced ahead of the auger-stripped drill rods using a modified pneumatic hammer placed horizontally in-line with the coring assembly.

This is the first use of a percussion coring method for drilling and coring horizontal boreholes. The drilling method allowed the collection of undisturbed cores with essentially 100% continuous core recovery over distances of 15 meters, both horizontally and vertically. The drilling techniques may soon be applied in other research projects in the SSP focused on natural heterogeneity and the bacterial transport. In addition, Tonto Drilling is currently applying the technology in characterization and cleanup effort at Los Alamos National Laboratory. Thus, the technology has applications in both basic research studies and applied technology projects.

Publication

F.J. Brockman, E.L. Majer, and F.J. Wobber. 1994. *Heterogeneity Subprogram: Five-Year Plan of Basic Research*. DOE Subsurface Science Program Document, U.S. Department of Energy, Washington, D.C.

Novel application of horizontal drilling and aseptic sampling and sample handling methods are used to determine subsurface microbial heterogeneity at the White Bluffs outcrop on the Columbia River. Research performed at the Pacific Northwest Laboratory.

Pacific Northwest Laboratory's Gulfstream 1 Hosts DOE/NN-20 Instrumentation

Principal Investigators: B.W. Wright, J.E. Smart, and W.R. Barchet

Funding Source: DOE/NN-20 Office of Research and Development (GC-01-01-09-6) and Office of Health and Environmental Research, Atmospheric Chemistry Program (KP-02-01)

The Gulfstream 1 (G-1) DOE Research Facility was equipped in FY 1995 with two instruments being developed for the Office of Research and Development in DOE/NN-20: the Air Concentrator-Ion Trap Mass Spectrometer (AC-ITMS) and the Real-Time Airborne Radionuclide Analyzer and Collector (R-TARAC). Both instruments are being developed for the third pod of the U.S. Department of Energy's Airborne Multisensor Pod System (AMPS) Program.

Flight tests were performed during the research and development phase of these instruments because the prototype instruments use sophisticated analytical concepts that have not been previously implemented in an aircraft environment. The prototype instruments, including their respective large-volume air samplers, were mounted inside the aircraft fuselage to provide easy access to the instruments. Installation required minor physical and electrical changes to the instruments to configure them for operation on the G-1.

The AC-ITMS provides both near real-time sample collection and mass spectrometric analysis of chemical compounds present in the atmosphere. The system applies to the analysis of volatile and semi-volatile organic and inorganic compounds, as well as compounds that can be thermally desorbed from particles. This portable system collects air samples at approximately 0.5 to $2.0 \text{ m}^3 \text{ min}^{-1}$ in a large-volume primary sorption unit for user specified time periods. After initial sample collection and concentration, the primary unit is isolated, and the sample is thermally desorbed and back-flushed to a secondary sorption unit for further sample concentration. Once transferred to the secondary sorption unit, the sample is again thermally desorbed, back-flushed, and directed to the ion trap mass spectrometer for analysis. Real-time

sample monitoring can also be performed directly with the mass spectrometer through a by-pass option on the primary collector unit.

The R-TARAC senses and collects radioactive particles in near real time from an airborne platform at $20 \text{ m}^3 \text{ min}^{-1}$ on filter cartridges. A high-sensitivity gamma spectrometer detects and records the energy spectrum of collected gamma-emitting radionuclides. The short-lived radionuclides detected include the organic and inorganic halogen radionuclides and the daughter products of the decay of the nobles gases (Xe, Ar, and Kr); all strongly associated with nuclear proliferation. Other short-lived radionuclides producing more than $10 \text{ disintegrations min}^{-1} \text{ m}^{-3}$ at gamma energies not overlapping those of radon daughter products can be detected. The R-TARAC is sufficiently sensitive to detect as few as $5,000 \text{ atoms m}^{-3}$ of a radionuclide with a half-life of 4 hours. Up to 18 filter cartridges can be stored in a removable canister for further post-flight analysis.

The flight tests provided valuable "hands-on" experimentation that could not be obtained by any other means. Key design concepts of the AC-ITMS and R-TARAC were evaluated under "real" operating conditions. Important air flow parameters, mechanical functions, and heating/cooling properties of the large-volume air samplers were characterized and evaluated. Unforeseen problems that occurred were corrected either immediately or prior to the next flight. The information obtained from these flight tests will be used for further design and operational optimization of these prototype instruments. Preliminary results represent encouraging progress for the operation and performance of the prototype AC-ITMS and R-TARAC instruments in an aircraft environment.

Air Concentrator-Ion Trap Mass Spectrometer (AC-ITMS)
RW Wright, Pacific Northwest Laboratory (509)376-1661

Real Time Airborne Radionuclide Analysis and Collection (RTARAC)
JE Smart, Pacific Northwest Laboratory (509) 376-8306

Pacific Northwest Laboratory's Gulfstream 1 Is Designated as a Department of Energy Research Facility

Principal Investigator: W.R. Barchet

Funding Source: Office of Health and Environmental Research, Atmospheric Chemistry Program (KP-02-01)

In FY 1995, the operation of PNL's Gulfstream 1 (G-1) moved from serving specific PNL projects to being a DOE Research Facility available to researchers throughout DOE's Atmospheric Chemistry Program. This facility is dedicated to the fulfillment of important DOE and national goals related to understanding atmospheric processes as they relate to the DOE's environmental missions and the global environment.

The G-1 is a large twin turboprop with performance characteristics of contemporary "in-production" aircraft. It is capable of measurements to altitudes approaching 30,000 feet over ranges of 1500 nautical miles, and can be operated at speeds that enable both relatively slow sampling and rapid deployment to field sites throughout the world. The aircraft is configured for versatile research applications. It accommodates a variety of external probes for aerosol and turbulence measurements and internal sampling devices for a wide range of measurements. The G-1 has sufficient cabin volume, electrical power and payload capabilities, and flight characteristics to accommodate a large variety of instrument systems and experimental equipment configurations. Internal instrumentation is mounted in removable racks that enables rapid reconfiguration as necessary. Data acquisition is performed by an on-board computer system that can accommodate a wide range of analog and digital inputs. Acquired data are processed post-flight to incorporate calibration data and user-specified formatting. Output can be provided on PC-compatible disks or magnetic tape in a format acceptable to the user.

Proposals stating research objectives and requesting aircraft time are reviewed by a DOE-empowered Research Aviation Facility Advisory Panel. The panel reviews the technical feasibility of the proposed research flights and makes recommendations to DOE on the award of flight hours. After the DOE awards flight hours, the research aircraft facility coordinates the approved requests and schedules flight time.

Although DOE/OHER provides flight hours without cost, projects using the facility must estimate the following costs of offsite aircraft logistics: 1) landing fees, 2) hangar rental, 3) ground support facilities, and 4) crew time and expenses for a PNL flight crew of two pilots and one engineer should be budgeted in the proposal. This information, along with the information provided in the Request for Aircraft Support Form, will be used in the review of the proposed request for flight hours.

The research aircraft facility **does not** cover the cost of engineering studies and airframe modifications needed for custom installation of project-specific instrumentation. Such costs must be paid by the user. The staff of the research aircraft facility will assist users in estimating these costs upon request. DOE covers all base operating costs (hangar rental and utilities, airport fees, calendar-based maintenance, flight crew training and proficiency maintenance, and flight crew and engineering staff hours) and all operating, maintenance, and logistical costs for up to 250 flight hours annually, including the off-site costs for the flight crew.

In FY 1995, the G-1 was used by researchers from several national laboratories (PNL, Argonne National Laboratory, Brookhaven National Laboratory) and universities (SUNY-Old Westbury, University of California-Irvine), and Battelle Columbus. It participated in the Nashville/ Middle Tennessee Valley field study of the multi-agency Southern Oxidants Study and carried out a field program in the northeastern United States for the Atmospheric Chemistry Program.

Publication

C.W. Spicer, D.V. Kenny, W.J. Shaw, K.M. Busness, and E.G. Chapman. 1994. "A Laboratory in the Sky: New Frontiers in Measurements Aloft." *Environ. Sci. Technol.* 28(9), 412A-420A.

Gulfstream 1 Designated a Department of Energy Research Facility

Radar Observations of the Mountain-Plain Wind System in the Rocky Mountains

Principal Investigators: C.D. Whiteman and X. Bian

Funding Source: Office of Health and Environmental Research, Environmental Sciences Division (KP-02)

In FY 1995, scientists at Pacific Northwest Laboratory used climatological analysis and wind data from two wind-profiling radars located on the east and west sides of the Rocky Mountains to detect a large-scale wind circulation associated with the Rocky Mountain cordillera. The large-scale wind system, known as the mountain-plain circulation, causes low-level air to converge over the Rocky Mountain crests during daytime. This convergence plays an important climatological role in the development of convective clouds and precipitation. A return circulation at upper levels of the atmosphere carries air back toward the plains. During nighttime, the direction of the circulation reverses. Then, low-level air drains down both sides of the Rocky Mountains and the resulting subsidence over the mountain crests draws air at upper levels from both the west and east sides of the mountains.

The mountain-plain circulation is well known in the Alps, where it was detected from climatological analyses of balloon ascents on the north and south sides of the Alps. The mountain-plain circulation in the Rocky Mountains has received little study, however, and the new research utilizes data from a new generation of continuously operating atmospheric wind-sensing Doppler radars that were installed as part of the National Oceanic and Atmospheric Administration's Wind Profiler Demonstration Network.

The climatological analyses, for the first time, allow a determination of the amplitudes and phases of the mountain-plain circulation over the Rocky Mountains, and further work with additional radar stations should allow a comprehensive investigation of this meteorologically important wind circulation.

The accompanying figure shows vertical profiles of the east-west diurnal wind components at stations on both the east and west sides of the Rocky Mountains at Platteville, Colorado, and at Aztec, New Mexico, respectively. Shown are results for two times of day—0800 and 1800 hours MST for the summer half-year (or warm season). These results were obtained from hourly wind data from two warm seasons using Fourier analysis. The circulation is seen to have an amplitude of about 1 m/s with a direction reversal at a level just above the Rocky Mountain crests.

Publication

C.D. Whiteman and X. Bian. 1995. "Radar Profiler Observations of Diurnal and Semidiurnal Wind Systems in the Rocky Mountains." Preprints, 7th Conference on Mountain Meteorology, 17-21 July 1995, Breckenridge, Colorado, 18-23.

EAST-WEST COMPONENT OF DIURNAL WINDS

Pacific Northwest Laboratory

RAFT Contaminant Transport Simulator Models Heterogeneous Subsurface Processes

Principal Investigator: A. Chilakapati

Funding Sources: Office of Health and Environmental Research, Subsurface Science Program (KP-02-03), and Environmental Management, Office of Technology Development

Recent research at Pacific Northwest Laboratory sponsored by OHER's Subsurface Science Program (SSP) has added a powerful new capability for modeling the complex biogeochemical reaction processes that occur during contaminant transport in the subsurface. Advances were made in the capabilities of the ReActive Flow and Transport (RAFT) simulator (which supported basic research in bacterial transport and intermediate-scale experiments in contaminant behavior) that found immediate application in support of EM-50's Plumes Remediation focus area at Hanford. Applications included 1) the use of RAFT to assist the design of an *in situ* bioremediation demonstration for simultaneous destruction of carbon tetrachloride and nitrate in the 200-West area, and 2) design of redox manipulation experiments for a subsurface chromium barrier at the 100-H and 100-D areas.

Advanced computational tools are being developed at PNL to investigate heterogeneous fundamental subsurface

reactive transport processes, many of which require predictions about solute interactions and microbiological activity at the molecular scale in the aqueous phase and at the aqueous-solid phase interface. Ongoing research will continually improve RAFT by, for example, describing kinetics of bacterial attachment and detachment, which may have a significant effect on mass balance of biodegradable contaminants and by explicitly accounting for solution density and viscosity.

Publication

A. Chilakapati. 1995. *RAFT. A Simulator for ReActive Flow and Transport of Groundwater Contaminants*. PNL-10636, Pacific Northwest Laboratory, Richland, Washington.

Multipoint Bioremediation Well
Three Views of Carbon
Tetrachloride Concentration

Isosurface is 95% of
Original Concentration

Multiport Bioremediation Well

Solar Semidiurnal Tides Discovered in Tropospheric Radar Data

Principal Investigators: C.D. Whiteman and X. Bian

Funding Source: Office of Health and Environmental Research, Atmospheric Studies in Complex Terrain Program (KP-02-01)

Investigators at Pacific Northwest Laboratory discovered unusual wind oscillations in climatological analyses of data from a new Doppler radar wind profiling device that was installed by the National Oceanic and Atmospheric Administration near the Grand Canyon in Arizona. Further investigation suggested that the oscillations, now observed in other radar records across North America, are solar thermal atmospheric tides. These tides are produced by absorption of the solar beam by ozone in the earth's stratosphere, and this mechanism for their formation produces a wind system that should be present over the entire globe. Such tides have been previously observed in the upper atmosphere (stratosphere and thermosphere) by geophysicists, but they have been poorly documented in the earth's lower atmosphere (troposphere) where they are much weaker, and where observational tools (e.g., twice-daily rawinsondes) are inadequate to properly resolve them in time and space. Since meteorological radar networks are now being installed in the U.S. and in other locations around the world, the new method of analyzing the tides using radar profiler wind data is expected to result in much new information on the solar tides. The tides are strong enough to affect some important aspects of the earth's climate, and may well have an effect on the timing and location of cloudiness and precipitation events.

Identification of the wind oscillations as solar thermal tides was pursued using both analyses and numerical modeling. The characteristics of the oscillations were first determined with harmonic analysis. The oscillations had unique characteristics that distinguish them from most tropospheric wind systems—they were semidiurnal, undergoing two, rather than one, complete oscillations per

day, and the winds turned clockwise with time at all altitudes. The oscillations had typical amplitudes of about 0.5 m/s. These tidal characteristics were found to match those predicted by a numerical model of the response of the earth's atmosphere to semidiurnal surface pressure oscillations that are known to be produced by solar tides. Further, the timing and global extent of the oscillations matched the model predictions.

The global solar tidal wind system can be illustrated using the two attached figures, which have been generated by the numerical model from observations of semidiurnal surface tidal pressure oscillations in hectopascals. The wind and pressure overlay, when placed on the global map, represents the wind and pressure perturbation patterns at midnight UTC. The propagation of this wind and pressure perturbation pattern around the globe can be illustrated by sliding the wind and pressure overlay from right to left across the globe, simulating the apparent movement of the sun from east to west. As the pressure and wind patterns move around the earth, the winds rotate clockwise above a point on the map to produce a semidiurnal wind oscillation of amplitude near 0.5 m/s.

Publications

C.D. Whiteman and X. Bian. 1995. "Radar Wind Profiler Observations of Solar Semidiurnal Tides." *Geophys. Res. Lett.* 22(8), 901-904

C.D. Whiteman and X. Bian. "Solar Semidiurnal Tidal Winds in the Troposphere: Detection by Radar Profilers." *Bull. Amer. Meteor. Soc.* 77(3) (in press).

Subsurface Recharge Rates and Natural Transport of Bacteria on the Regional Scale

Principal Investigators: E.M. Murphy and T.R. Ginn

Funding Source: Office of Health and Environmental Research, Subsurface Science Program (KP-02-03)

Geochemists, microbiologists, and modelers at Pacific Northwest Laboratory are testing geochemical and microbiological approaches to studying natural recharge rates through unsaturated zones. These approaches will help us gain information about bacterial transport in the subsurface that is applicable to bioremediation design and to performance assessments of low-level waste sites and the Department of Energy's deep nuclear repository for periods of 10,000 years.

Atmospheric chloride was used as a tracer to evaluate the movement of water through the unsaturated zone of soil and subsoil at the Hanford Site in southeastern Washington State in order to estimate bacterial transport from surface to depth. A model was developed to evaluate the unsaturated zone flow processes that affect the chloride profile with depth. Trace concentrations of a second atmospheric tracer, iodine-129 (byproduct of plutonium processing starting ~1945) produced a sharp pulse in the sediment profile. The depth of this pulse was directly related to a short-term (50-year) recharge rate. The advantage of these methods is that they provide low-cost, site-specific recharge estimates. These recharge estimates are being used for performance assessment modeling at Hanford to predict risk of human exposure from low-level waste over time periods ranging up to 10,000 years.

Additionally, in collaboration with Florida State University, the University of Tennessee, and Rensselaer Polytechnic Institute, PNL scientists used aseptic drilling

and sampling methods to compare vertical profiles of microbial communities at sites with high and low natural recharge rates. Analysis of ratios of ester-linked phospholipid fatty acids (PFAs) extracted from bacterial membranes in the sediment samples indicated that PFAs from common surface organisms as well as ones that are induced by stress occurred at greater depth, indicating that downward movement of cells may be associated with natural recharge.

Publications

T.R. Ginn and E.M. Murphy. "Generalized Chloride Mass Balance: Forward and Inverse Solutions for One-Dimensional Tracer Convection Under Transient Flux." (submitted).

E.M. Murphy, T.R. Ginn, and J.L. Phillips. "Geochemical Estimates of Recharge in the Pasco Basin: Evaluation of the Chloride Mass-Balance Technique." (submitted).

T.J. Phelps, E.M. Murphy, S.M. Pfiffner, and D.C. White. 1994. "Comparison Between Geochemical Biological Estimated of Subsurface Microbial Activities." *Microbial Ecology* 28: 335-339.

K.A. Schramke, E.M. Murphy, and B.D. Wood. 1995. "The Use of Geochemical Mass-Balance and Mixing Models to Determine Groundwater Sources." *Applied Geochemistry* (in press).

Subsurface Microbial Respiration Rates From Geochemistry and Isotope Fractionation

Down Gradient ↓	Groundwater		Terminal Electron Acceptor			
	Recharge to:	Age	O ₂	SO ₄ ⁻²	Fe ³⁺	MnO ₂
			(mmol/L/y)			
	Aiken	modern	2.2 x 10 ⁻³	-0-	-0-	-0-
	Aiken to:					
	P-29	~200	1.6 x 10 ⁻⁴	6.4 x 10 ⁻⁵	1.8 x 10 ⁻⁴	9.0 x 10 ⁻⁷
	P-26	5510	1.4 x 10 ⁻⁶	2.6 x 10 ⁻⁶	1.2 x 10 ⁻⁴	8.3 x 10 ⁻⁸
	P-24	5750	8.1 x 10 ⁻⁶	1.3 x 10 ⁻⁶	6.9 x 10 ⁻⁶	7.6 x 10 ⁻⁸

Results of geochemical reaction modeling are used to determine microbial respiration rates along groundwater flow paths established by geochemical carbon-14 dating. In this "in situ" approach, the consumption of electron acceptors in the system (mmole/L/yr), a measure of metabolism, is modeled and verified at the Savannah River Plant.

Pacific Northwest Laboratory

Effect of Recharge on Microbial Transport in the Vadose Zone

Comparison of vadose zone microbial communities with depth at Hanford sites with high and low groundwater recharge rates shows that low recharge associated with high topography is correlated with older pore water ages and greater microbial diversity. This reflects lower rates of vertical microbial transport and longer periods of time for in situ evolution of diverse communities

Pacific Northwest Laboratory

Transport and Diffusion of Hazardous Material from the Rocky Flats Plant: Determining the Effects of Winds from Local Canyons

Principal Investigator: J.C. Doran

Funding Source: Environmental Sciences Division (KP-02-01-00-0)

In the late summer and fall of 1993, a three-month measurement campaign was carried out in Colorado's Front Range near the Department of Energy's Rocky Flats Plant (RFP). Using sodars and radar wind profilers, scientists in DOE's Atmospheric Studies in Complex Terrain (ASCOT) program sought to determine the characteristics of nocturnal drainage flows from Eldorado Canyon, which lies to the northwest of RFP, and to investigate the circumstances under which these flows might affect the local wind conditions at RFP. The issue is important because the airborne transport and diffusion of hazardous material that might be released from RFP depends sensitively on the wind and temperature conditions in the first 100 meters above the surface. These conditions, in turn, are often governed by the complex terrain of the Front Range immediately to the west of RFP, but predicting just how and when the terrain effects will be manifested is difficult. Moreover, existing meteorological monitoring networks and emergency response models in use at RFP are not adequate to describe some of the possible influences of air flow from the local canyons.

Pacific Northwest Laboratory scientists were part of the multilaboratory team formed to acquire wind data in the RFP area in 1993, and have since been engaged in the analysis and interpretation of those data. The sodar records from that time period show that nocturnal thermally enhanced down-valley flows from Eldorado Canyon can be usefully classified as either irregular, with intermittent shallow flows and peak winds occurring in the lowest 150 to 200 meters near the canyon mouth, or well developed, with moderate to strong winds extending over depths of 400 meters or more. Under irregular wind regimes, there is little evidence that the local winds at RFP are affected by Eldorado Canyon winds; during periods of well-developed canyon winds, there is a greater likelihood of a canyon influence.

A numerical mesoscale model was used to obtain an understanding of the mechanisms responsible for the differences in canyon flows. By varying the ambient wind and temperature conditions in the model simulations, a series of sensitivity tests were conducted to determine the range of circumstances most likely to result in well-developed flows out of Eldorado Canyon and to assess their probable effects at RFP. It was found, from numerical simulations and from an analysis of rawinsonde data obtained from Stapleton Airport near Denver, that well-developed flows in Eldorado Canyon are often preceded by deep (approximately 3000 meters or more), well-mixed afternoon boundary layers over the plains adjacent to the Front Range. Such conditions are common during the summer and early fall so that the probability of Eldorado Canyon winds affecting the local meteorology at the RFP can be significant. Further, by injecting passive tracer particles into the wind and turbulence fields generated by the numerical model, it was possible to follow the paths of air parcels that originated in Eldorado Canyon and subsequently flowed out over the plains to the east. The trajectories confirm the likelihood that canyon winds could affect the dispersion of hazardous material released from RFP, especially if material were released at heights greater than approximately 50 meters. Thus, emergency response systems designed for RFP area should be capable of accounting for outflows from the nearby canyons, a capability that is currently lacking.

Publication

J.C. Doran. "The Influence of Canyon Winds on Flow Fields near Colorado's Front Range." *J. Appl. Meteor.* (accepted).

Simulated paths of marker particles released in Eldorado Canyon drainage and flowing over the Rocky Flats Plant. Contour intervals are in m.

Pacific Northwest Laboratory

KP-03 Health Effects

Genetics of Radon-Induced Lung Cancer

Principal Investigators: J.D. Saffer and K.M. Groch

Funding Source: Office of Health and Environmental Research (KP-03-02)

Naturally occurring radon gas is the largest single source of radiation exposure to the general public and is responsible for about 10% of all lung cancers. Ongoing research at Pacific Northwest Laboratory into the health effects of residential levels of radon has indicated that an individual's genetic makeup may contribute to the risk of radon-induced lung cancer. PNL scientists have shown that 1) mouse strains are differentially susceptible to radon- (alpha-particle-) induced lung cancer, 2) the difference is not how much stable chromosome damage is induced, but rather how the tumors progress from benign to malignant character, and 3) there are pre-existing differences in the level of expression of several genes in the lung tissues from these mice that may be responsible for the differential sensitivity.

Epidemiological studies of underground miners indicate that inhaled radon is carcinogenic and extrapolating these data to the general public exposed in residences suggests that about 10% of all lung cancers may be due to this exposure. There is also a growing body of evidence suggesting that the risk of "spontaneous" cancer in humans has a genetic component and that the increased risk of cancer following exposure to ionizing radiation is relative to the underlying risk of "spontaneous" disease. Importantly, epidemiological studies indicate a genetic component to "spontaneous" lung cancer. If the risk of radon-induced lung cancer is also relative to the risk of "spontaneous" disease, identifying and characterizing the gene or genes responsible will provide molecular probes for identifying individuals at increased risk of radiogenic lung cancer as well as important insights into the cellular and molecular bases for the pathogenesis of lung cancer in general.

The work is important for two reasons. First, improving the energy efficiency of new and existing homes typically results in decreased fresh air exchange raising the possibility of increased levels of radon gas in the home environment. Identifying individuals having a risk of radon-induced lung cancer greater than the "average" individual in the general population will provide one additional parameter for more rational decision making regarding acceptable radon levels. Just as importantly, lung cancer, regardless of cause, is a major health problem and identifying the cellular and molecular bases for the pathogenesis of this disease in the context of radon-induced cancer will add to the body of knowledge directly applicable to identifying appropriate therapeutic strategies.

The future directions of the work include first mapping the chromosomal location of the mouse gene or genes modifying the tumor response to inhaled radon and then cloning and characterizing the sequences. We will then make use of the information emerging from the Human Genome Project to identify whether similar genes exist in human populations. Additionally, we are in the process of characterizing the genes that are differentially expressed in the lung tissues of the two strains currently under evaluation. These genes will also be cloned and characterized for use in identifying whether the corresponding human genes are involved in the pathogenesis of human lung cancer.

Publication

K.M. Groch, M.A. Khan, A.L. Brooks, and J.D. Saffer. "Differential Lung Tumor Response to Radon and Urethane in A/J and C57BL/6J Mice." (in preparation).

Biology & Chemistry Department
Pacific Northwest Laboratory

Radon Contributes to the Progression of Lung Tumors to a More Cancerous State

Size distribution and tumor type (open circles, hyperplastic lesions and adenomas; closed circles, carcinomas) of lung lesions found in A/J mice 60 weeks following exposure to radon. The data show that radon exposure results in a spontaneously-occurring tumors becoming malignant (carcinomas).

Biology & Chemistry Department
Pacific Northwest Laboratory

Differential Sensitivity to Radon-induced Lung Cancer Is Not Due to Differential Amounts of DNA Damage

Micronuclei frequency, an indicator of chromosome breakage, in deep-lung cells isolated from A/J (radon-sensitive) and C57BL/6J (radon-insensitive) mice following exposure to 300 WLM radon and progeny, an equivalent exposure to ore-dust carrier only, and injection with ethyl carbamate (a chemical carcinogen). The data show that DNA damage caused by radon in the two mouse strains is equivalent and does not reflect the differential tumor incidence between the strains.

Influence of Dose Distribution on Cell/Cell Communication

Principal Investigators: A.L. Brooks, S. Bao, L. Braby, N. Metting, and R. Jostes

Funding Source: Office of Health and Environmental Research (KP-03-02)

The major problem remaining in radiation biology is understanding the risk associated with low-level exposure to alpha particles either from the nuclear industry or from residential radon exposure. Pacific Northwest Laboratory researchers have modified an accelerator in a way to develop a single particle/single cell irradiation device (microbeam). With this unique instrument, PNL researchers can determine the relationships between responses from "hot particles" exposure which occurs when isotopes like $^{239}\text{PuO}_2$ are inhaled and very low doses such as those from radon inhalation. This project uses the microbeam to expose individual cells to defined numbers of alpha particles.

Since it has been reported that more cells in a population respond following a low dose of alpha particles that have been traversed by alpha particles, it was suggested that the cells communicate the damage to other cells that can then make a biological response. If this is the case, then the target size for alpha exposure is not the cell nucleus but may be as large as several cells. This would change the modeling of damage from radon and plutonium and other alpha emitting radionuclides. PNL researchers use the unique microbeam combined with cellular and molecular biology expertise to define the induction of cytogenetic damage by exposure of single cells to defined numbers of alpha particles. These studies are being expanded to determine the requirements for cell/cell communication of damage and will help define the mechanisms involved in the interactions induced in hit cells with that in non-hit cells. Such studies will also be very helpful in understanding the potential synergistic interactions such as observed between cigarette smoking and radon exposure.

The studies at PNL will define how many cells in a population need to be hit by an alpha particle and the level or number of hits required for that cell to communicate its damage to the neighboring cells. Such information can help in understanding the risk from exposures to radon in homes since in the home-exposure environment each respiratory cell will receive no more than a single alpha traversal during its lifetime.

The key questions remaining in this area are 1) the shape of the dose response curve at very low doses (i.e., a single alpha particle delivered to a single cell) and 2) the cellular and molecular requirements for the communication of cellular damage from one cell to another and how this communication alters the response of the cells and the risk for induction of disease. Information on these questions is being derived at PNL by combining the unique single cell exposure system with the cellular and molecular biology in a way that will help us understand risk.

Publication

J.M. Nelson, A.L. Brooks, N.F. Metting, M.A. Khan, R.L. Buschbom, A. Duncan, R. Miick, and L.A. Braby. "Effects of Defined Numbers of 3.2 MeV Alpha Particles on Individual Mammalian Cells." *Radiation Research* (submitted).

Biology & Chemistry Department
Pacific Northwest Laboratory

Single Radiation Events Cause Chromosome Damage

CHO cells were exposed to defined numbers of particles and the frequency of micronuclei, a measure of chromosome breakage, determined in binucleated cells. It was determined that a single alpha particle is capable of inducing a significant increase in the frequency of micronuclei and the hit-response relationship observed was similar to the dose-response relationships for other alpha emitting radionuclides.

Molecular Events During Tumor Initiation

Principal Investigator: D.L. Springer

Funding Source: Office of Health and Environmental Research (KP-03-02)

Individuals are exposed to cancer-causing agents from a variety of sources including chemicals that result from combustion of fossil fuels and atmospheric changes that increase ultraviolet (UV) intensity. Since these exposures may lead to cancer in some individuals, it is important to understand the molecular mechanisms responsible for repair of DNA damage produced by these materials. Work at the Pacific Northwest Laboratory has taken advantage of a unique cellular model containing a gene that functions in either the active or inactive state thereby providing an experimental tool to evaluate the relationship between DNA repair and transcription. Results from this research have provided unequivocal evidence for coupling of DNA repair to transcription. Ultimately these results will contribute to the scientific basis for identification of susceptible individuals so that biochemical information can be used to set occupational exposure limits.

Development of disease is believed to result from exposure, genetic susceptibility, and endogenous variables. Even though a great deal of effort has gone into exposure assessment, very little research has been conducted to develop methods that will allow us to identify individuals who are susceptible to DNA damaging agents and ultimately cancer. Because of the need for biochemical information to set occupational exposure limits, efforts at PNL have focused on DNA repair processes and the relationship between repair and transcription. Information suggesting an association between DNA repair and transcription has developed over the past few years but until now was incompletely understood because the major thrust of other researchers' studies compared repair in two genes, one active and the other inactive.

Even though it is increasingly clear that DNA repair of UV-induced photoproducts is associated with transcription, very few studies have been conducted to determine whether similar coupling occurs for bulky chemical adduct damage. To fill this gap we are using a mouse cell line transfected with an inducible gene. Growth of these cells in the presence of a glucocorticoid hormone activates transcription while in the absence of the hormone

the gene is silent. This molecular switch provides a tool to study DNA repair when the gene is transcriptionally active or inactive. To evaluate this, cells are damaged with a chemical carcinogen at concentrations that nearly eliminate transcription. When the cells are in a transcriptionally active state the gene is rapidly repaired, as measured by return of transcription, to 60% of control levels in 24 hours, whereas when the cells are in a transcriptionally inactive state, the gene is repaired more slowly with transcription returning to 15% of control levels within 24 hours. Additionally, we find that this inhibition of gene transcription in cells is dose dependent and follows first-order kinetics. Interestingly, UV damage in this model is repaired in both the transcriptionally active and inactive states. Conversely our results indicate that bulky chemical adducts are efficiently removed only during transcription. Although both of these types of damage are repaired by the same pathway, the mechanism for these differences has not been identified and is the subject of future studies.

These results demonstrate that the rate of repair is significantly enhanced when cells are transcriptionally active suggesting a strong coupling between transcription and repair. Further, results from this work provide the rationale for proposed structure/function studies of nucleotide excision repair. Since the vast majority of cellular DNA is associated with proteins, it is critical that both the biochemical and structural studies include DNA-histone interactions of the nucleosome and other higher levels of organization of chromatin. We anticipate that these studies will increase our understanding of why certain sites are preferentially repaired and how the processes contribute to an individual's susceptibility to disease.

Publication

B.D. Thrall, D.B. Mann, M.J. Smerdon, and D.L. Springer. 1994. "Nucleosome Structure Modulates Benzo[a]pyrene Diol Epoxide Adduct Formation." *Biochemistry* 33, 2210-2216.

Biology & Chemistry Department
Pacific Northwest Laboratory

Gene Transcription Is Coupled to DNA Repair

Transcript levels, indicative of how much a gene is being used, were measured at different times after damage of the gene by a chemical carcinogen. The closed circles are for cells treated with a hormone that activates the gene, whereas open circles are for cells not treated with hormone. The data show that the transcription blocking DNA damage in this gene is efficiently removed only when the cells were activated with the hormone, that is, the repair is coupled to transcription.

Statistical Analyses of Data from Radiobiologic Animal Studies

Principal Investigators: E.S. Gilbert, E. Hui, and R. Scherpelz

Funding Source: Office of Health and Environmental Research (KP-03-02)

The objectives of statistical analyses conducted under this project are to provide measures of carcinogenic risk that can be appropriately compared across studies, to quantify differences in risks produced by different radionuclides and different exposure conditions, to compare risks across species, to investigate the shapes of dose-response functions in a consistent manner, and to evaluate the consistency of results with models that have been used for human radiation risk assessment. These analyses will provide information that is needed for estimating human risks, and will thus decrease the uncertainty in risk estimates, especially for exposure situations not represented by human data.

A wide variety of radiobiologic animal experiments, primarily in rodents and beagles, have been conducted for the Department of Energy at several laboratories. These experiments were designed to obtain information for exposure situations where adequate human data are unavailable, and particularly to provide information on how dose, dose rate, dose distribution, linear energy transfer, and other factors modify risks. The data from these experiments represent an extremely important resource, and the recent development of powerful statistical tools and software now makes it feasible to provide a more rigorous and informative assessment of these data than has been possible in the past. This project is a collaborative effort among statisticians at the Pacific Northwest Laboratory, the Inhalation Toxicology

Research Institute (ITRI), and Argonne National Laboratory to increase understanding of radiation-related human health risks by providing this assessment.

Since this project was initially funded in FY 1994, analyses of data from several studies have been conducted. Analyses of rats exposed to radon and radon progeny at PNL have demonstrated that the inverse exposure-rate effect is limited to animals exposed at levels higher than 1000 WLM (working level month), a finding that has important implications for determining risks from residential radon exposures. Preliminary analyses comparing lung tumor risks in dogs exposed to inhaled $^{239}\text{PuO}_2$, $^{238}\text{PuO}_2$, and $^{239}\text{Pu}(\text{NO}_3)_4$ at PNL have indicated that both the magnitude of the risk (per unit of dose) and the shape of the dose-response function may differ for the three radionuclides. If borne out by planned future analyses that address bone and liver tumor risks and that combine data from experiments conducted at PNL and ITRI, these findings could be important in setting standards for exposures to these radionuclides.

Publication

E.S. Gilbert, W.C. Griffith, and B.A. Carnes. 1995. *Statistical Methodology Used in Analyses of Data From DOE Experimental Animal Studies*. PNL-10659, Pacific Northwest Laboratory, Richland, Washington.

Steps in Carcinogenesis: The Effects of Very Low Doses of High LET Radiation on Specific Cell-Cycle-Regulating Proteins

Principle Investigators: N.F. Metting and L.A. Braby

Funding Source: Office of Health and Environmental Research and NASA (KP-03)

Researchers at Pacific Northwest Laboratory have visualized the location of specific cell-cycle regulatory proteins within individual mammalian cells using immunofluorescence microphotometry and confocal laser scanning microscopy. By contrasting measurements in irradiated versus unirradiated cells, the epigenetic consequences of radiation damage in the short term are being studied for the ultimate purpose of gaining insight into the process of carcinogenesis.

Measurements of the intracellular localization of several cell-cycle regulatory proteins in the human cervical carcinoma cell line, HeLa S3, clearly show that the protein resides in the cytoplasm throughout interphase (G1, S, and G2 phases), then moves into the nucleus at the beginning of mitosis (M-phase, in which chromosomes condense and form daughter nuclei). Measurements in the normal primary human cell strain, AG1521, show that after x-irradiation, cyclin B1 can be found in both nucleus and cytoplasm during the period of G2 arrest. The phenomenon of radiation-induced division delay, like tumor induction, is characterized by disruption of normal growth regulation, and involves many of the same regulatory proteins. It is clear that at least two important cell-cycle arrest points exist in mammalian cells, one in G1-phase, just before the beginning of DNA-synthesis, and the other in G2-phase, just before mitosis. In particular, the transition from G2-phase into mitosis in dividing mammalian cells is dependent on the kinase activity of the cdc2-cyclin B protein complex. Western blot analysis of cultures irradiated by moderate doses of x-rays or alpha particles showed a transient failure of the

complex to activate, by way of dephosphorylation of the cdc2 subunit, which correlated with the duration of radiation-induced G2-arrest. The data support the hypothesis that radiation-induced delay in cdc2 activation is caused by, or affects, alteration of the normal cellular compartmentalization of the proteins.

An understanding of the mechanisms of cell-cycle regulation and therefore the potential for disrupting normal regulation when certain mutations occur, is an important component of the information needed to evaluate health risks of radiation and other environmental pollutants.

In the coming weeks, synchronized cells will be irradiated through the nucleus using the PNL single particle irradiator, to explore possible explanations for the higher level of cell-cycle arrest seen for high linear energy transfer (LET) radiations by the measurement of changes in localization after the passage of one or more alpha particles through the cell.

Publications

N.F. Metting, A.M. Koehler, H. Nagasawa, J.M. Nelson, and J.B. Little. 1995. "Design of a Benchtop Alpha Particle Irradiator." *Health Phys.* 68(5), pp 1-6.

N.F. Metting and J.B. Little. 1995. "Transient Failure to Dephosphorylate the cdc2-Cyclin B1 Complex Accompanies Radiation-Induced G2-phase Arrest in HeLa Cells." *Radiation Research* 143, pp 286-291.

Cyclin B1 Immunostaining in Normal Human Skin Fibroblasts.

In these pictures, cyclin B1 is shown in green, the DNA is shown in red. Notice that the interphase cells irradiated by 2 Gy X-Rays are unable to exclude cyclin B1 from the nucleus, unlike the control cells. This occurrence is shown in yellow. These measurements also support the earlier observations from western blot analysis (see graph above) that showed an increase in cyclin B levels as a function of dose.

The Use of In Vitro/In Vivo Techniques to Develop Methods to Define Biologically Effective Dose from Radon Exposure

Principal Investigators: A.L. Brooks, S. Bao, K. Groch, and R. Jostes

Funding Source: Office of Health and Environmental Research (KP-03-02)

Radon is an alpha emitter that is present in the environment. It is responsible for more than 50% of the total environmental radiation dose and has a negative impact on indoor air quality. This large environmental exposure results in an increase in the calculated respiratory tract cancer risk. Setting radiation standards to control exposure to this isotope and its daughters are based on human data from uranium miners. Pacific Northwest Laboratory scientists are making it possible to determine the relationship between exposure and effective radiation dose to the cells of the respiratory tract. With such information it is possible to extrapolate between the dose and damage which resulted from radon exposure in mines to that which is present following residential exposure and reduce the uncertainty associated with radon risk estimates in residents.

Research has been conducted at PNL to define the relationship between the biological damage induced in cells in culture to that produced in animals following inhalation of radon and its progeny. We have developed methods to expose cells and animals to radon or to low linear energy transfer radiation like gamma rays from ^{60}Co , to isolate cells from different regions of the respiratory tract, to grow these cells in short-term tissue culture, and to evaluate the frequency of damaged chromosomes using the micronucleus assay. PNL research has demonstrated that the use of a biological indicator or exposure dose and damage makes it possible to validate mathematical models of radon deposition and determine the influence of exposure conditions and cell types on the induction of cellular damage associated with cancer induction. We have determined that deep lung fibroblasts and deep lung epithelial cells have the same radiation sensitivity to the exposure of gamma rays from ^{60}Co but that the deep lung epithelial cells have greater damage per unit of exposure following radon inhalation. This suggests that the radon delivers a larger effective dose to the epithelial cells which are at a higher risk for the induction of cancer than to the fibroblasts.

PNL research also has wide applications in evaluating the effective dose to different cell types in the respiratory

tract following inhalation of chemicals as well as radiation. With the large number of inhalation studies being conducted at PNL, the expansion of this technique can provide information on exposure/dose relationships and information on the mechanisms of chemical damage in production of the early events during cancer induction.

The key questions for the future are to define how the exposure environment influences effective cellular dose and cancer risk. Studies are being extended from the use of uranium ore dust which was similar to the environments found in mines to the use of aerosols and the exposure conditions found in residential exposures. These studies will help define risk from low doses found following residential radon exposure. Linking biology and aerosol physics make it possible to test a range of physical models of deposition and to convert environmental exposure conditions to effective dose and risk to individual respiratory tract cells.

Publications

A.L. Brooks, M.A. Khan, A. Duncan, R.L. Buschbom, R.F. Jostes, and F.T. Cross. 1994. "Effectiveness of Radon Relative to Acute ^{60}Co Gamma-Rays for Induction of Micronuclei in vitro and in vivo." *Int. J. Radiat. Biol* 66, 801-808.

A.L. Brooks, R. Miick, R.L. Buschbom, M.K. Murphy, and M.A. Khan. 1995. "The Role of Dose Rate in the Induction of Micronuclei in Deep-Lung Fibroblasts in vivo After Exposure to Cobalt-60 Gamma Rays." *Radiation Research* 144, 114-118.

M.A. Khan, F.T. Cross, R.L. Bushbom, and A.L. Brooks. 1995. "Inhaled Radon-Induced Genotoxicity in Wistar Rat, Syrian Hamster, and Chinese Hamster Deep-Lung Fibroblasts in vivo." *Mutation Research* 334, 131-137.

M.A. Khan, F.T. Cross, R.F. Jostes, E. Hui, J.E. Morris, and A.L. Brooks. 1994. "Micronuclei Induced by Radon and Its Progeny in Deep-Lung Fibroblasts of Rats in vivo and in vitro." *Radiation Research* 139, 53-59.

R.C. Miller, M. Richards, D.J. Brenner, E.J. Hall, R.F. Jostes, T.E. Hui, and A.L. Brooks. "The Biological Effectiveness of Radon-Progeny Alpha Particles. V. Oncogenic Transformation from Monoenergetic Accelerator-Produced Alpha Particles Compared with Polyenergetic Alpha Particles from Radon Progeny." *Radiation Research* (in press).

M. Nagarkatti, P.S. Nagarkatti, and A.L. Brooks. "Effect of Radon on the Immune System: Alterations in the Cellularity and Functions of T Cells in Lymphoid Organs of Mouse." *J. Toxi. and Environ. Health* (in press).

Biology & Chemistry Department
Pacific Northwest Laboratory

Radon Causes More Damage to Epithelial Cells than to Fibroblasts in the Deep Lung

The induction of micronuclei, a measure of chromosome breakage, is shown for different exposures of radon. Working Level Months (WLM) are a measure of total radon exposure. The data show that the amount of damage in the deep lung epithelial cells is much greater than the damage to the deep lung fibroblasts. This finding suggests a higher risk to these cells per unit exposure.

KP-04 General Life Sciences

Analysis of Oligonucleotide Mixtures by Electrospray Ionization-Mass Spectrometry

Principal Investigator: R.D. Smith

Funding Source: Office of Health and Environmental Research, Human Genome Program (KP-04)

Our aim is to develop electrospray ionization mass spectrometry (ESI-MS) methods for high speed DNA sequencing of oligonucleotide mixtures, that can be integrated into an effective overall sequencing strategy. ESI produces intact molecular ions from DNA fragments of different size and sequence with high efficiency (Smith et al., *Anal. Chem.* [62]882-889). Our aim is to determine mass spectrometric conditions that are compatible with biological sample preparation and that avoid problems due to dissociation, aggregation, or adduction during ionization of the DNA fragments. Oligonucleotide ions are typically produced from ESI with a broad distribution of net charge states for each molecular species (i.e., $(M-nH)^n$, where n is a series of integers), and thus leading to difficulties in analysis of complex mixtures. To make identification of each component in a sequencing mixture possible, the charge states of molecular ions can be reduced by manipulating the ESI process and/or by using gas-phase reactions. The charge-state reduction methods being examined include 1) reactions with organic acids and bases (in the solution to be electrosprayed and the ESI-MS interface or the gas phase), 2) the labeling of the oligonucleotides with a designed functional group for production of molecular ions of very low charge states, and 3) the shielding of potential charge sites on the oligonucleotide *phosphate/phosphodiester* groups with polyamines (and the subsequent gas-phase removal of the neutral amines). In initial studies two methods for charge-state reduction of gas phase oligonucleotide negative ions have been tested: 1) the addition of acids and bases to the oligonucleotide solution and 2) the formation of diamine adducts followed by dissociation in the interface region. In the first method, the efficiency of charge-state reduction depends on the pK^a , the concentration and the nature of the acids. Acetic and formic acids

were found to be better reagents than HCl, CF_3CO_2H and H_3PO_4 ; however, suppression of the analyte solution was observed. If the infused solution contained a high percentage of organic solvent, signal suppression was obviated. The addition of organic bases reduced cation adduction and unexpectedly was found to reduce charge-states. The second method has the advantage that the stability of oligonucleotides is not affected but requires the optimization of the interface dissociation conditions and the amounts of diamine added to the oligonucleotide solution which may not be analytically reproducible. Both methods show promise for charge-state reduction and results have been demonstrated for several small oligonucleotides (i.e., $d(pT)_{12}$, $d(AGCT)$, $d(pT)_{18}$, $d(pC)_{12}$, $d(pA)_6$, and 8-mers of A, C, and T). Substantial reduction in the spectral density was observed for a three-, four-, and six-component mixture of oligonucleotides sprayed from a solution containing a charge-state reducing agent. Our aim is to provide a basis for the development of an overall approach to high speed sequencing to provide a basis for the subsequent step of prototyping a cost-effective high-throughput instrument for broad application.

Publications

X. Cheng, D.C. Gale, H.R. Udseth, and R.D. Smith. 1995. "Charge State Reduction of Oligonucleotide Negative Ions from Electrospray Ionization." *Anal. Chem.* (67)586-593.

D.C. Muddiman, X. Cheng, R.D. Smith. "Charge-State Reduction with Improved Signal Intensity of Oligonucleotides in Electrospray Ionization Mass Spectrometry." *J. Am. Soc. Mass Spectrom.* (submitted).

High Speed Sequencing of Single DNA Molecules in the Gas Phase by FTICR-MS

Principal Investigator: R.D. Smith

Funding Source: Office of Health and Environmental Research, Human Genome Program (KP-04)

This project is aimed at the development of a totally new concept for high speed DNA sequencing based upon the analysis of single (i.e., individual) large DNA fragments using electrospray ionization (ESI) combined with Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. In our approach, large single-stranded DNA segments extending to as much as 25 kilobases (and possibly much larger) are first transferred to the gas phase using ESI. The multiply charged molecular ions are trapped in the cell of an FTICR mass spectrometer, where one or more *single ion(s)* can be selected for analysis. The mass-to-charge ratio (m/z) is rapidly and nondestructively measured during the analysis. Single ion detection is achievable due to the high charge state of the electrosprayed ions and the unique sensitivity of the FTICR mass spectrometer developed at Pacific Northwest Laboratory.

Our efforts under the first several years of this project have demonstrated the capability for the formation and extended trapping, isolation, and monitoring of sequential reactions of highly charged DNA molecular ions with molecular weights well into the megadalton range. We have shown that large multiply charged individual ions of both single and *double-stranded* DNA anions can also be efficiently trapped in the FTICR cell, and their mass-to-charge ratios measured with very high accuracy. Thus, it is feasible to quickly determine the mass of each lost unit as the DNA is subjected to rapid reactive degradation steps. Our aim is to now develop methods based upon the use of ion-molecule or photochemical processes that can promote a stepwise reactive degradation of gas-phase DNA anions. Successful development of one of these approaches could greatly reduce the cost and enhance the speed of DNA sequencing, potentially allowing for sequencing *DNA segments of more than 25 kilobases* in length, on a time-scale of minutes with negligible error rates, with the added potential for conducting many such

measurements in parallel. *The techniques* being developed promise to lead to a host of new methods for DNA characterization, potentially extending to the size of much larger DNA restriction fragments (>500 kilobases).

Publications

J.E. Bruce, X. Cheng, R. Bakhtiar, Q. Wu, S.A. Hofstadler, G.A. Anderson, and R.D. Smith. 1994. "Trapping, Detection, and Mass Measurement of Individual Ions in a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer." *J. Amer. Chem. Soc.* (116)7839-7847.

R. Chen, X. Cheng, D.W. Mitchell, S.A. Hofstadler, A.L. Rockwood, Q. Wu, M.G. Sherman, and R.D. Smith. 1995. "Trapping, Detection and Mass Determination of Coliphage T4 DNA (1.1×10^8 Da) Ions by Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry." *Anal. Chem.* (67)1159-1163.

R. Chen, Q. Wu, D.W. Mitchell, S.A. Hofstadler, A.L. Rockwood, and R.D. Smith. 1994. "Direct Charge Number and Molecular Weight Determination of Large Individual Ions by Electrospray Ionization-Fourier Transform Ion Cyclotron Resonance Mass Spectrometry." *Anal. Chem.* (66)3964-3969.

X. Cheng, R. Bakhtiar, S. Van Orden, and R.D. Smith. 1994. "Charge State Shifting of Individual Multiply-Charged Ions of Bovine Albumin Dimer and Molecular Weight Determination Using an Individual-Ion Approach." *Anal. Chem.* (66)2084-2087.

R.D. Smith, X. Cheng, J.E. Bruce, S.A. Hofstadler, and G.A. Anderson. 1994. "Trapping, Detection and Reaction of Very Large Single Molecular Ions by Mass Spectrometry." *Nature* (369)137-139.

Rational Enzyme Redesign: Improving Biodehalogenation

Principal Investigator: R.L. Ornstein

Funding Source: Office of Health and Environmental Research (KP-04)

In this project we studied the structure-function-dynamics relationships of biodehalogenating microbial enzymes. Recent experiments have demonstrated that cytochrome P450cam effectively binds and dehalogenates several heavily chlorinated ethanes under anaerobic conditions; but this enzyme is ineffective against 1,1,1-trichloroethane (TCA) (the number two Department of Energy priority halocarbon in subsurface soils/sediments and groundwater). We wish to gain a better understanding of the underlying structure-function-dynamics relationships in order to use this information to rationally redesign P450cam to improve the dehalogenation of TCA and other target halocarbons. The results of this research could hasten in situ bioremediation of recalcitrant, heavily-chlorinated compounds in deep subsurface environments.

In principle, the functional characteristics of an enzyme may be changed by appropriate amino acid changes. Since all possible combinations of amino acid changes for even the smallest enzyme cannot be made, the essential question is which ones to make. Answering this question requires a thorough understanding of the underlying structure-function-dynamics relationships for an enzyme. Applying molecular dynamics simulations to a high-resolution, experimental three-dimensional enzyme structure can yield valuable and unique structural and dynamic information that can greatly expand the range of rational and testable hypotheses (that would not be evident from a consideration of only the experimental structure[s]). Molecular dynamics simulations on cytochrome P450cam with bound camphor analogues indicate that Phe 87 can adopt multiple conformations resulting in a significant increase in the active site volume and in active site plasticity not evident from the x-ray structure (Paulsen et al. 1991; Bass et al. 1992); additional simulations of the P450cam mutant Phe 87 to Trp predicted this specific substitution as a key element for improving the binding and turnover of loose-fitting camphor analogues (Bass et al. 1992). It is thus interesting to note that Sligar and coworkers have recently observed that this active-site cytochrome P450cam mutant (Phe 87 to Trp) dechlorinates pentachloroethane approximately three times faster than the wild-type enzyme. Our recent molecular dynamics simulations reveal that the mutant enzyme binding pocket remains smaller than the native enzyme, and that pentachloroethane assumes configurations closer to the heme-Fe in the F87W mutant twice as

often as in the wild-type enzyme. These results taken together with the experimental observations of Wackett and coworkers that solutions containing wild-type P450cam dehalogenate pentachloroethane 100 times faster than those containing free heme (Li and Wackett 1993) suggest that mutants could be developed to further improve the binding interactions leading to enhanced dehalogenation. Not surprisingly, molecular dynamics simulations have shown that TCA is highly mobile in the active site of native P450cam, indicating that its residence time near the heme Fe may be quite low.

In comparison to camphor, norcamphor is also highly mobile in the active site of P450cam, largely because norcamphor is missing three methyl groups that are present in camphor. We have previously predicted by molecular dynamics simulations that changing the active site residue Thr 185 to Phe would significantly reduce the mobility of norcamphor and should result in greater regiospecificity and more efficient product formation; this prediction was experimentally confirmed (Paulsen et al. 1993). Both P450cam residues Phe 87 and Thr 185 are on the "ceiling" of the active site in a position on top of the catalytic heme group. We therefore performed molecular dynamics simulations of TCA-bound to three different mutant forms of P450cam: 1) Phe 87 to Trp, 2) Thr 185 to Phe, and 3) both Phe 87 to Trp and Thr 185 to Phe. These mutations add steric bulk to regions of the active site left void when the native substrate, camphor, is replaced with the much smaller TCA molecule. Comparison with the wild-type trajectory indicates that TCA interacts significantly more frequently with the heme Fe in only the double mutant. It is noteworthy that we also explored the possible impact of one triple mutant that contained the double mutant noted above but also added additional bulk to one of the "side walls" of the active site. This triple mutant slightly reduced the interaction between TCA and the heme Fe. We are currently awaiting the outcome of the experiments that challenge these predictions. Moreover, it is important to note that simulations permit us to see enzymes after they "relax" in the absence of crystal packing forces. In certain cases, we have already seen large relaxations for the enzymes cytochrome P450BM-3 and T4 lysozyme. As computer power increases, we expect to see, for the first time, other enzyme substrates that will only become accessible with longer simulations. Studying such fundamental structure-function-dynamics relationships of key enzymes will

improve our basic understanding and lead to improved rational redesign for bioremediation and other technological purposes.

Publications

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P.J. Loida. 1994. Ph.D. Thesis: University of Illinois at Urbana-Champaign.

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J.I. Manchester and R.L. Ornstein. "MD Simulations Indicate that F87W,T185F Cytochrome P450cam May Reductively Dehalogenate 1,1,1-Trichloroethane." *J. Biomol. Struct. Dyn.* 12 (in press).

J.I. Manchester, M.D. Paulsen, R. Rein, and R.L. Ornstein. "1,1,1-Trichloroethane-Bound Cytochrome P450cam Dynamics; Does Active Site Water Make a Difference?" *Chem. Phys.* (in press).

M.D. Paulsen and R.L. Ornstein. 1994. "Active Site Mobility Inhibits Reductive Dehalogenation of 1,1,1-Trichloroethane by Cytochrome P450cam." *J. Comput.-Aided Molec. Design* 8, 389-404.

M.D. Paulsen and R.L. Ornstein. 1995. "Dramatic Differences in the Motions of the Mouth of Open and Closed Cytochrome P450bm3 by MD Simulations." *Proteins* 21, 237-243.

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M.D. Paulsen, D. Filipovic, S.G. Sligar, and R.L. Ornstein. 1993. "Controlling the Regiospecificity and Coupling of Cytochrome P450cam: T185F Mutant Increases Coupling and Abolishes 3-Hydroxy-norcamphor Product." *Protein Science* 2, 357-365.

Comparison of X-ray Crystal and Molecular Dynamics Simulated Active Sites for Wild and Double-Mutant Cytochromes P450cam with Bound 1,1,1-Trichloroethane

Comparison of X-ray Crystal and Molecular Dynamics Structures of the Residues Controlling the 'Mouth' of the Active Site of Cytochrome P450BM-3

Pacific Northwest Laboratory/Rational Enzyme Redesign/PI:RL Ornstein

KP-05 ARM Program

Atmospheric Radiation Measurement Program Advances

ARM Chief Scientist/Technical Director: G. Stokes/T. Cress
Funding Source: Environmental Sciences Division (KP-05)

The Pacific Northwest Laboratory hosts the Program Office for the Department of Energy Atmospheric Radiation Measurement (ARM) program, a multilaboratory effort to improve the performance of General Circulation Models (GCMs) used for climate prediction. The ARM program focuses on improving the models and algorithms used in GCMs to represent the radiative energy transfer processes in the atmosphere including the impact of clouds on these processes. ARM is a field measurement program designed to deliver data enabling the development and testing of a new generation of more accurate and representative radiative and cloud process models. ARM is the first program to make this type of data available. Dramatic improvements in the performance of GCMs used for climate prediction and research are expected.

Data characteristic of the most significant and stressing climatic regions of the earth are required to develop and test these new radiative models. During the past year ARM introduced newly developed instrumentation at its mid-latitude Southern Great Plains site and built a semi-autonomous station for routine measurements in remote tropical locations in the Pacific Ocean basin. The first ARM Atmospheric Radiation and Cloud Station (ARCS) will be shipped to the island of Manus in Papua New Guinea in January 1996. A variant of the ARCS concept is being designed for use in hostile high-latitude conditions. The first instrumentation for arctic measurements will be deployed in the area of Point Barrow, Alaska, in 1997.

This fall the ARM program is conducting at the Southern Great Plains site its largest field program to date. The objective of ARESE (the ARM Enhanced Shortwave

Experiment) is to resolve a major discrepancy in our understanding of the atmosphere's shortwave (solar) radiation balance. This field measurement program involves newly developed instrumentation, the ARM Unmanned Air Vehicle program, the high flying NASA ER-2 aircraft, and specialized instrumentation from other collaborating programs and universities. Resolution of the shortwave radiation balance has the potential of being a most significant advance in the development of more accurate climate prediction models.

New measurement capabilities developed for routine field data acquisition include

- Raman Lidar—measures the vertical profile of water vapor in the atmosphere, a difficult and critical variable for radiative processes
- Digital day-night whole-sky imager—quantitatively documents cloud characteristics
- Unmanned Air Vehicles—function as long endurance measurement platforms over the ARM sites to complement ground measurements.

These efforts are representative of the multilaboratory/multiagency/university collaborative efforts being pulled together by the Program Office: the Raman Lidar was developed by Sandia National Laboratories based on a prototype instrument developed by the National Aeronautics and Space Administration's Goddard Space Flight Center; the Whole Sky Imager was developed by the University of California at San Diego; and the Unmanned Air Vehicle Program Office at Sandia National Laboratories works in close collaboration with the ARM program.

Atmospheric Radiation Measurement Program

Atmospheric Radiation Measurement Program Advance in Cloud Radiation Modeling

ARM Chief Scientist/Technical Director: G. Stokes/T. Cress
Funding Source: Environmental Sciences Division (KP-05)

Based on extensive cloud data available from the Atmospheric Radiation Measurement (ARM) program, a significant advance in modeling the interaction of solar radiation with clouds has been made by ARM Science Team investigator Warren Wiscombe and his research group at the National Aeronautics and Space Administration's Goddard Space Flight Center. This work provides an explanation for the observed differences between the variation of liquid water in clouds and the corresponding variation of reflected solar radiation. The difference is due to previously unaccounted for horizontal radiation transfer within the cloud.

According to the prevailing theory, the variation of radiation reflected from clouds was expected to behave in the same way as the variation of liquid water within the clouds, as indicated by the green line labeled "Simple Theory" in the accompanying figure. However, high-resolution satellite data from LANDSAT indicated that at small scales the variations in the reflected radiation diminished much more rapidly than predicted. (The red line labeled "Reflected Radiation from Clouds" in the figure.) The question was, does cloud liquid water vary differently at small scales than at large scales thereby producing the observed change in the radiation variation, or are there additional radiative processes that are unaccounted for?

Dr. Wiscombe's group utilized the extensive measurements of cloud liquid water from ARM's groundbased microwave radiometers and ARM-sponsored aircraft to

determine its variation at much finer scales than previously possible. As shown in the accompanying figure (by the blue line labeled "ARM Cloud Liquid Water Data"), this variation agrees with the established theory.

Dr. Wiscombe's group then sought a theoretical explanation for the difference in the behavior of the reflected radiation.

In the short term, this work provides an improved model of reflected solar radiation from clouds. In addition, it is being adapted to improve laser-radar (LIDAR) remote sensing of cloud properties. In the longer term, this work is expected to lead to improvement in the critical area of cloud/radiation interaction in models of the atmospheric general circulation applied to global climate change issues.

Publications

A. Davis, A. Marshak, R. Cahalan, and W. Wiscombe. "Horizontal Radiative Fluxes in Stratocumulus and the Landsat Scale-Break." *J. Atmos. Sci.* (submitted).

A. Marshak, A. Davis, W. Wiscombe, and R. Cahalan. "Radiative Smoothing in Fractal Clouds." *J. Geophys. Res.* (accepted).

A. Marshak, A. Davis, W. Wiscombe, and G. Titov. 1995. "The Verisimilitude of the Independent Pixel Approximation Used in Cloud Remote Sensing." *Remote Sens. Environ.* 52, 72-78.

Fundamental Radiative Smoothing Scale

⬡ indicates Radiative Smoothing Scale around 200 - 300 m

- ◆ Above this scale, radiance follows fluctuations of cloud structure
- ◆ Below this scale, radiation field is smoother than predicted

Dr. Wiscombe's group at NASA/GSFC found an explanation of the above "scale break" in terms of smoothing by horizontal radiative fluxes using multiple scattering theory and fractal cloud models based on ARM and other cloud liquid water data.

Two important applications of this study

- (1) Development a new method for simulating satellite data at scales smaller than 200 m;
- (2) Adaptation of LIDAR techniques to infer cloud's density, thickness and degree of homogeneity.

Atmospheric Radiation Measurement Program Advance in Longwave Radiation Modeling

ARM Chief Scientist/Technical Director: G. Stokes/T. Cress

Funding Source: Environmental Sciences Division (KP-05)

A significant advance in modeling the terrestrial infrared (longwave) radiation spectrum has been made by Atmospheric Radiation Measurement program Science Team investigators using the extensive data available from the ARM program. This work has achieved agreement between measured and modeled spectra at the level identified as necessary for modeling global climate change.

Doubling the atmospheric concentration of carbon dioxide is expected to result in an increased net radiative flux at the earth's surface of 4 W/m^2 . Consequently, radiation transport models must be accurate to this level or better. The Inter Comparison of Radiation Codes in Climate Models (ICRCCM) showed that the less complex radiation models employed in climate models did not achieve this accuracy when compared with more complex line-by-line (LBL) models. Furthermore, the accuracy of the reference LBL models was unknown due to the unavailability of measurements for comparison.

To address this problem, ARM has deployed a high-accuracy interferometer specially designed by the Space Science and Engineering Center at the University of Wisconsin - Madison for measuring longwave radiance spectra over the range $500 \text{ to } 3000 \text{ cm}^{-1}$ ($3.3 \text{ to } 20 \text{ }\mu\text{m}$) at 0.5 cm^{-1} resolution. A sample spectrum is presented in an accompanying figure with the primary atmospheric contributor indicated for each spectral region. Such spectra are acquired at 10-minute intervals on a continuing basis.

In order to fully utilize the vast amount of spectral data being acquired by ARM, Pacific Northwest Laboratory

staff have collaborated with researchers at Atmospheric and Environmental Research (AER), Inc. to implement the AER line-by-line model in the ARM data system. This has enabled model spectra to be computed automatically, up to eight per day, using measurements of the vertical distribution of temperature and water vapor from the ARM Cloud and Radiation Testbed (CART) facility in Oklahoma. These computed spectra are automatically subtracted from the corresponding measured spectra and the differences integrated over each atmospheric contributor to the radiance. The statistics from these comparisons permit the source of any discrepancies between the model and the spectral data to be readily identified. These results are available to all ARM Science Team investigators to help guide their research.

Some results of this comparison are presented in an accompanying figure. These results show that the radiance contribution from water vapor and ozone emission lines are well modeled over a wide range of atmospheric water vapor amounts. (One particular advantage of ARM's long-term measurements is the large annual range of water vapor in Oklahoma.) Greater uncertainty is indicated in the "transparent" regions—the regions between the emission lines. These differences are believed to be due to aerosols which grow in size with increasing amounts of water vapor. Aerosol data from instrumentation presently being installed at the ARM CART are expected to significantly improve the model performance in this region.

Measured Downwelling Radiance at the Surface

(Measured - Model) vs. Precipitable H₂O

Development of Guidelines for the Voluntary Reporting of Greenhouse Gases under Section 1605(b) of the Energy Policy Act of 1992

Principal Investigators: K. Richards and E. Malone
Funding Source: Policy Office (KP-05)

PNL staff were involved in the development and publication of guidelines for voluntary reporting of greenhouse gas emissions, emissions reductions, and carbon sequestration. The guidelines take the form of a three-volume, approximately 400-page publication.

The federal government has increasingly turned to voluntary and cooperative programs to encourage the private sector to exercise environmental stewardship. This program was mandated by Congress in the Energy Policy Act of 1992 to address fears that companies that reduced current emissions would be disadvantaged if they ever came under mandatory emissions reduction because of erosion of their baseline emissions levels. Development of the guidelines involved balancing the many conflicting interests of government agencies, private sector firms and nongovernmental organizations. We used extensive workshops to encourage private sector and NGO input to the process. While the voluntary nature of the program meant we were not technically required to follow the formal rulemaking process, we found that doing so added

credibility to the process. The process of guideline development demonstrated that the technical hurdles and the political/organizational issues are inextricably intertwined.

This project established DOE at the forefront of agencies doing voluntary programs for environmental protection. It served as a springboard for the Department's involvement in the U.S. Initiative on Joint Implementation, an international program developed in response to the 1992 Framework Convention on Climate Change. Many of the technical issues from the 1605(b) project regarding how the greenhouse gas impacts of individual projects should be evaluated are now being applied to the development of a handbook for the USJI program.

Publication

Guidelines for the Voluntary Reporting of Greenhouse Gases under Section 1605(b) of the Energy Policy Act of 1992 (General Guidelines, Volume I and Volume II).

The Effects of Spatially Varying Surface Fluxes on the Predictions of Climate Models

Principal Investigators: J.C. Doran, J.M. Hubbe, J.C. Liljegren, W.J. Shaw, and S. Zhong

Funding Source: Environmental Sciences Division (KP-05)

Numerical models used to study factors that may affect climate are an important element of the Department of Energy's Atmospheric Radiation Measurement (ARM) program. One of the potential limitations of these models is the coarse scale at which they operate; grid cells of 100 kilometers on a side or larger are common and phenomena with characteristic scales smaller than the grid size cannot be explicitly resolved. Pacific Northwest Laboratory scientists have been studying how the failure to resolve spatially varying surface fluxes of heat and moisture will affect the predictions of the models of the properties of the lower atmosphere, such as the depth of the turbulent mixed layer and the likelihood of cloud formation.

Using data obtained from ARM's Cloud and Radiation Testbed (CART) site in Oklahoma and Kansas, they developed a method to obtain an estimate of the flux values over the full 300 km x 350 km site at a resolution of $(6.5 \text{ km})^2$. A numerical mesoscale model with this same resolution was then run using a distribution of surface flux values similar to those measured over the CART site. Simulated values of mixed-layer depths and relative humidity were compared with corresponding quantities obtained from a model run with uniform

surface fluxes. Despite some differences in the two sets of results, the location of likely areas of cloud formation were surprisingly similar.

Additional tests will be carried out in the coming year using a range of atmospheric and flux conditions. If similar results are found, this would imply that the effects of inhomogeneous surface fluxes are not as large as has been suggested in other studies. Those studies used idealized distributions of surface characteristics that may have produced unreasonably large variations in the simulated surface flux values. When more realistic flux conditions based on actual observations are specified, the performance of coarse resolution models does not appear to be so adversely affected. Such a result would remove a significant source of uncertainty in climate models.

Publication

J.C. Doran, J.C. Liljegren, and S. Zhong. "Spatially-Varying Surface Fluxes at the Southern Great Plains CART Site and Their Effects on Boundary-Layer Properties." Preprints, Seventh Symposium on Global Change Studies, Atlanta, Georgia, January 28-February 2, 1996. American Meteorological Society, Boston, Massachusetts.

The Great Plains Low-Level Jet

Principal Investigator: S. Ghan

Funding Source: Office of Health and Environmental Research, Atmospheric Studies in Complex Terrain Program (KP-05-04-00-0)

The fundamental issue in the Department of Energy's Atmospheric Radiation Measurement (ARM) program is the development and testing of radiative transfer and cloud parameterization schemes for global climate models. The ARM's Southern Great Plains Cloud and Radiation Testbed (CART) is centered in an area that is strongly impacted by a prominent meteorological phenomenon—the Great Plains Low-Level Jet (LLJ). The LLJ plays a vital role in cloud formation and precipitation over the CART site. A full understanding of the LLJ and its impact on clouds and precipitation is crucial for the success of the ARM program.

Using data from state-of-the-art radar wind profilers, a state-of-the-art numerical mesoscale model, and a community climate model, scientists at PNL have carried out a comprehensive study of the LLJ and its impact on the meteorology and climatology over the Southern Great Plains CART and surroundings. We have achieved, through comprehensive data analysis and numerical modeling, a better understanding of the physical mechanisms for the development and evolution of the

LLJ. We have found that the LLJ produces a significant diurnal cycle in vertical motion and moisture convergence at the leading edge of jet core where convective clouds usually occur. We have also found that the current global climate models do not simulate the relationships between the LLJ and clouds and precipitation, and therefore, there is an urgent need to develop a parameterization scheme that incorporates the effect of the LLJ in the climate models. The development and evaluation of such a parameterization scheme is now under way.

Publications

S. Ghan, X. Bian, and L. Corsetti. "Simulation of the Low-Level Jet by General Circulation Models." *Monthly Weather Review* (submitted).

S. Zhong, J.D. Fast, and X. Bian. "A Case Study of the Great Plains Low-Level Jet Using Wind Profiler Network Data and a High Resolution Mesoscale Model." *Monthly Weather Review* (submitted).

The Great Plains Low-Level Jet

A Case Study Using Wind Profiler Network Data and A Mesoscale Model

S. Zhong, J.D. Fast, X. Bian, and C.D. Whiteman
Pacific Northwest Laboratory

Observation

Simulation

MiniCAM Integrated Assessment Model Development

Principal Investigators: J. Edmonds, R. Brown, C. MacCracken, H. Pitcher, N. Rosenberg, and M. Wise

Funding Source: Office of Health and Environmental Research, PE, Electric Power Research Institute (KP-05)

The field of integrated assessment (IA) has developed rapidly over the past few years. IA for climate change examines the full range of natural and social science issues in an integrated, interdisciplinary manner. One of the earliest and most influential models to be developed has been the MiniCAM. The MiniCAM is a reduced form model that covers anthropogenic emissions from the full range of human activities including energy production and use, and from agriculture and land-use. This model was the first integrated assessment model to include sulfur aerosols explicitly (Edmonds et al. 1993). The model showed the surprising result that temperatures were higher over the first half of the next century under extreme emissions reductions scenarios than under the business as usual scenarios, due to the cooling effects of sulfur emissions interacting with the concurrent carbon emissions.

The model has also been used to examine the cost of implementing the Framework Convention on Climate Change (FCCC) goal of stabilizing the concentrations of greenhouse gases (Richels and Edmonds 1993). This work has led to the surprising conclusion that it may be half as expensive to stabilize CO₂ concentrations than it is to stabilize CO₂ emissions. This result coupled with the finding that advanced energy technology development and deployment holds the promise of low cost emissions reductions (Edmonds et al. 1993), has profound implications for implementing the Berlin Mandate (Edmonds and Wise 1995).

Publications

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J. Edmonds, M. Wise, and C. MacCracken. 1994. *Advanced Energy Technologies and Climate Change: An Analysis Using the Global Change Assessment Model (GCAM)*, PNL-9798, UC-402. Pacific Northwest Laboratory, Richland, Washington.

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T.M.L. Wigley, R. Richels, and J. Edmonds. 1995. "Stabilizing CO₂ Concentrations: The Choice of Emissions Pathway." *Nature* (submitted).

Global Annual Energy Production and Use

Comparison of Emission Trajectories Consistent with Various Atmospheric CO₂ Concentrations Developed by the IPCC (S350-S750) by Wigley, Richels, and Edmonds (S350a-S750a)

Global Annual Fossil Fuel CO₂

A One-Dimensional Model for the Parameterization of Deep Convection in the Ocean

Principal Investigators: T. Paluszkiwicz and L.F. Hibler

Funding Source: Computational Hardware, Advanced Mathematics, Model Physics Program (KP-05-03)

Deep convection plays an important role in the global ocean circulation, transporting near-surface water to great depths and helping form the deep and intermediate waters of the ocean. This redistribution of heat throughout the ocean is a key component in linking the ocean thermohaline cycle with global scale atmospheric cooling. The current generation of ocean general circulation models (OGCMs) do not properly represent the process of oceanic deep convection. The improved representation of key climate-related processes in ocean and coupled ocean-atmosphere circulation models is one of the goals of the Department of Energy's, Computer Hardware, Advanced Mathematics and Model Physics (CHAMMP) Program. Motivated by the need for OGCMs to better model the production of deep and intermediate water masses, oceanographers from Pacific Northwest Laboratory's Marine Sciences Laboratory have developed a one-dimensional penetrative plume model to parameterize the process of deep convection in OGCMs.

The ocean plume parameterization scheme (OPPS) takes the temperature and salinity profiles of OGCM grid boxes and simulates the subgrid-scale effects of convection using a one-dimensional parcel model. The one-dimensional model moves water parcels from the surface layer down to their level of neutral buoyancy, simulating the effect of convective plumes. While in transit, the plumes exchange water with the surrounding environment; however, the bulk of the plume water mass is deposited at the level of neutral buoyancy. Weak upwelling around the plumes is included to maintain an overall mass balance. The process continues until the available buoyant energy of the one-dimensional vertical column is minimized. The parameterized plume entrainment rate, which plays a central role in the model physics, is calculated using modified equations based on Turner's (1976) entrainment hypothesis. This scheme differs from the convective adjustment techniques currently used in OGCMs because the parcels penetrate downward without the appropriate degree of mixing with the environment, until they reach their level of neutral stability.

The OPPS was tested using observations from the Greenland and Labrador Seas. Initial results indicated that the parameterization correctly simulates the evolution of deep convective mixing on the appropriate time scale. The ocean plume parameterization scheme was then tested on a larger, regional scale by incorporating OPPS into the OGCM, testing the model, and then evaluating the OGCM with OPPS against the OGCM with the standard convective adjustment algorithm. These tests indicated that OPPS performed well and improved the simulation of convective events when the model simulation was evaluated against theoretical results. We have recently completed the optimization of OPPS for inclusion in the massively parallel ocean circulation models. The next series of tests will be conducted on larger scale (global models) and tracer values will be used to evaluate the correctness of OPPS in simulating convection. Simulated tracer ages will be compared with observed tracers to evaluate the performance of the models.

The future direction of the research is to develop an integrated wind- and buoyancy-forced surface mixed-layer parameterization in order to improve the representation of vertical fluxes of mass through the mixed layer and deep convection forced by both buoyancy flux and wind mixing.

Publications

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OPPS MIXING

A. For shallow plumes, exchange between adjacent layers to reduce ABE to 0

B. Deep plumes entrain fluid from layers that they move through

C. Displacement and upwelling in environment

D. Detrainment of plume water in lower levels

E. Weighted average of plume and environment yields adjusted profile

$\theta(^{\circ}\text{C})$ at 75°N and Day 85
 Heat Flux = 100 W/m^2 , Latent Heat Flux = 30 W/m^2
 UNESCO Eq. of State

Second Scientific Assessment of the Intergovernmental Panel on Climate Change

Principal Investigators: R. Moss, J. Edmonds, S. Rayner, K. Richards, and M. Scott

Funding Source: Office of Health and Environmental Research, PE (KP-05)

Five Pacific Northwest Laboratory staff actively participated in development and completion of the Intergovernmental Panel on Climate Change (IPCC) Second Assessment Report (SAR).

The most active participant was Richard Moss who headed the Technical Support Unit (TSU) for the IPCC Working Group II (WGII). As such Dr. Moss was responsible for seeing that the largest and most ambitious of the three SAR components was completed successfully. Because the United States was co-chair of WGII, Dr. Moss' position was highly visible, and the successful conclusion of the WGII report can be credited in no small measure directly to Dr. Moss' efforts.

Jae Edmonds also participated in the IPCC SAR, working as a Lead Author on three chapters of Working Group III (WGIII), and two chapters of WGII. Mike Scott, a Convening Lead Author, held a position that carries with it the responsibility for delivering a peer reviewed chapter to the Technical Support Unit for publication. Dr. Scott's chapter on the impacts of climate change on human settlements is regarded as one of the best. In addition, Steve Rayner and Ken Richards also contributed to the assessment in WGII and WGIII respectively.

Much of the work of PNL was highlighted in the IPCC. Earlier work by PNL staff was heavily utilized in the recently released IPCC report, *Climate Change 1994*:

Radiative Forcing of Climate Change and An Evaluation of the IPCC IS92 Emission Scenarios. This retrospective evaluation showed the relationship between the IPCC IS92 emissions scenarios and other independent researchers. In general, the group found that the range of global emissions scenarios adequately reflected the range in the open literature. However, variation in published open literature regional and national emissions scenarios were sometimes different than those found in the IS92 scenarios. The writing team concluded that future IPCC efforts should approach the problem of scenario development in an entirely different manner. The IPCC should eschew the notion of developing "official" scenarios, and open the process to the full range of scientists working in the field.

Publications

J. Alcamo, A. Bouwman, J. Edmonds, A. Grübler, T. Morita, and A. Sugandhy. 1995. "An Evaluation of the IPCC IS92 Emission Scenarios." in *Climate Change 1994: Radiative Forcing of Climate Change and An Evaluation of the IPCC IS92 Emission Scenarios*. Cambridge University Press, London.

The IPCC Second Assessment Report. Cambridge University Press, Cambridge, United Kingdom. (in press).

Turbulence Modeling in the Ocean: Simulation of the Surface Mixed Layer and the Formation of Deep Water from Convection

Principal Investigators: D.W. Denbo and E.D. Skylvingstad
Funding Source: Environmental Sciences Division (KP-05)

The purpose of our research is to increase the understanding of ocean processes that are important for accurate climate modeling. In ocean general circulation models, many processes, such as deep water formation, mixing in the thermocline, ice-ocean interactions, and surface exchange, are poorly represented. Results from the surface mixed layer and deep water formation studies are being used to improve the parameterizations of these processes.

Surface mixed layer research at Pacific Northwest Laboratory centers on the simulation and measurement of turbulence in the upper 10 to 100 meters of the ocean. These experiments demonstrate the importance of surface waves and subsequent Langmuir circulations on defining the turbulence structure of the mixed layer and the rate at which the mixed layer deepens. These are important parameters for global climate modeling because the mixed-layer depth is critical in determining the sea-surface temperature, which is a primary variable in coupling the atmosphere and ocean heat budgets. Recent experiments have focused on the simulation of the western tropical Pacific Ocean. Warm water in this region of the Pacific is a key heat source for climate oscillations such as the El Nino/Southern Oscillation. Our results show how westerly windburst events decrease the sea-surface temperature in this region, which is a common precursor for the onset of El Nino events.

Deep convection, important in moderating the uptake of CO₂ by the ocean and in the meridional circulation, which affects climate by transporting heat from the tropics to the polar regions, motivates this research. Numerical experiments were conducted to examine the structure, onset, and strength of penetrative plumes, which are capable of moving surface waters relatively unchanged to great depths. These experiments have provided valuable information that has been used to develop a parameterization of deep convection for use in ocean general circulation models. Current research centers on the sensitivity of convection to changes in the surface forcing parameters such as heat flux and evaporation. We have also performed experiments to study the basic principals of turbulence modeling, namely, the impact of resolution on the accuracy of the models. These simulations show that the model accuracy increases with higher resolution, but in a nonlinear fashion. Doubling the resolution does not lead to a halving of the model error.

The ocean large-eddy simulation model (OLEM) is presently being run on a small, onsite multiprocessor SparcServer, the CM-S at Los Alamos, and the Cray C90 at the National Energy Research Supercomputer Center.

Schematic Ocean Mixed Layer

Simulated Ocean Mixed Layer

Donald W. Denbo
Pacific Northwest Laboratory

Donald W. Denbo
Pacific Northwest Laboratory

Laboratory Directed Research and Development

Advanced Mass Spectrometric Methods for Structural Biology Research

Principal Investigator: R.D. Smith

Funding Source: Laboratory Directed Research and Development

New methods have been developed and demonstrated for the study of noncovalent biopolymer interactions of direct relevance to structural biology, biotechnology, bioremediation, and health effects research. Fourier transform ion cyclotron resonance (FTICR) mass spectrometry with electrospray ionization has been shown capable of transferring non-covalent protein-DNA and protein inhibitor complexes from solution to the high vacuum FTICR ion trap where the complex and its constituents can be characterized.

Studies of both single and double stranded DNA in non-covalent complexes with proteins have demonstrated that electrospray ionization (ESI)-FTICR methods can be used to examine intact protein-DNA complexes from solution, and that strong binding oligonucleotides can be readily distinguished from others displaying weak binding. In particular, protein-DNA complexes can be examined in competitive binding experiments without adverse effects due to weaker non-specific interactions, as shown in the first figure.

In additional studies we have shown that combinatorial libraries of small molecules can be tested in one experiment to establish the relative binding for library constituents with a selected protein target. The generation and searching of large combinatorial libraries has become popular for certain classes of compounds for the purposes of drug discovery. In the combinatorial approach, mixtures are synthesized and subsequently examined for their affinity to a targeted biopolymer. An essential aspect of screening large libraries of compounds is the ability to identify the active components on the basis of their strong binding to the selected target. Initial studies demonstrating our approach for the identification of species from combinatorial libraries have been conducted in collaboration with Professor George Whitesides (Harvard University), who has developed bovine carbonic anhydrase (BCA) inhibitors based on a benzene sulfonamide core structure with a variety of substituent groups attached. An important and novel aspect of our approach involves the identification of the individual binding species by the dissociation of the complexes in the FTICR ion trap followed by their further characterization in the same experiment by high resolution and multi-stage methods. To demonstrate the use of larger combinatorial libraries, a mixture of para-substituted benzene

sulfonamide inhibitors was examined in which all combinations of 17 amino acid residues were incorporated into two positions ($17 \times 17 = 289$ components). The complexes in the ion trap were dissociated, and the resulting spectra allowed the inhibitors to be identified (see the second figure). Importantly, these preliminary results allow the relative binding affinities of the inhibitors to be obtained, as shown in the third figure. Among the broad potential applications of these new methods are studies of DNA-protein interactions processes in which binding to repair enzymes from large mixtures of damaged DNA is used to understand the initial damage recognition step in DNA repair.

Publications

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X. Cheng, R. Chen, J.E. Bruce, B.L. Schwartz, G.A. Anderson, S.A. Hofstadler, D.C. Gale, R.D. Smith, J. Gao, G.B. Sigal, M. Mammen, and G.M. Whitesides. "Using Electrospray Ionization Mass Spectrometry to Study Competitive Binding of Inhibitors to Carbonic Anhydrase." *J. Amer. Chem. Soc.* (in press).

X. Cheng, S.A. Hofstadler, J.E. Bruce, A.C. Harms, R. Chen, R.D. Smith, P.N. Goudreau, and T.C. Terwilliger. *Electrospray Ionization with High Performance Fourier Transform Ion Cyclotron Resonance Mass Spectrometry for the Study of Noncovalent Biomolecular Complexes.* Techniques in Protein Chemistry VI, R.H. Angeletti, Ed., Academic Press (in press).

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Q. Gao, X. Cheng, R.D. Smith, C.F. Yang and I.H. Goldberg. "Binding Specificity of Post-Activated Neocarzinostatin Chromophore Drug-Bulged DNA Complex Studied Using Electrospray Ionization-Mass Spectrometry." *J. Mass Spectrom.* (submitted).

B.L. Schwartz, D.C. Gale, R.D. Smith, A. Chilkoti, and P.S. Stayton. 1995. "Investigation of Noncovalent Ligand Binding to the Intact Streptavidin Tetramer by Electrospray Ionization Mass Spectrometry." *J. Mass Spectrom.* 30, 1095-1102.

X. Cheng, A.C. Harms, P.N. Goudreau, T.C. Terwilliger, and R.D. Smith. "Direct Measurement of Oligonucleotide Binding Stoichiometry of Gene V Protein by Mass Spectrometry." *Proc. Natl. Acad. Sci.* (submitted).

PU.1 Protein Binds to dsDNA with Recognition Sequence GGAA/T

PU.1 + 17-bp dsDNA (wild type)
with recognition sequence

PU.1 + 17-bp wild type + 20 fold excess of
19-bp w/o recognition sequence (mutant)

$(1:1)_w = 1:1$ complex of PU.1 with wild type dsDNA

$(1:1)_m = 1:1$ complex of PU.1 with mutant dsDNA

*Collaboration with Paul E. Morin of University of Toronto, Canada

ESI-FTICR mass spectra of the PU.1 protein in competitive binding experiments with a double stranded 17 bp oligonucleotide having the GGA(A/T) recognition sequence with a 1.3 fold excess (left) and a 20 fold excess (right) of a 19 bp oligonucleotide without the recognition sequence. The results show binding for only the DNA with the recognition sequence and that the intact complex can be detected with high resolution and sensitivity, and that the expected solution specificity of binding is reflected by the mass spectrometric results.

Dissociation of Selected 9- Charge State Complexes of BCaII with 289 Inhibitors

A demonstration of bioaffinity characterization methods used with a combinatorial library. BCA-inhibitor complexes were isolated in the FTICR ion trap, and these precursors were dissociated to yield protein ions and singly charged inhibitors (bottom). The middle and top panels show that the inhibitors detached from the enzyme can be analyzed by high resolution FTICR.

Relative Binding Affinity to BCAll for 289-Component Inhibitors from Mass Spectrometry

AA1, AA2: 17 out of 20 natural amino acids
(excluding Cys, Met, and Trp)

Projected relative binding affinities with BCA for the components of the 289-component combinatorial library of inhibitors, determined from the experiment shown in Figure 2.

Development of Advanced Techniques: Rapid Analysis of Strontium-90 by Automated Sequential Injection Analysis

Principal Investigators: J. Grate, J. Janata, and R. Strebin
O. Egorov and J. Ruzicka, University of Washington
Funding Source: Laboratory Directed Research and Development

Scientists at Pacific Northwest Laboratory, working in collaboration with scientists at the University of Washington, have developed a new automated microscale instrument for determining the concentration of strontium-90 in radioactive wastes. The new instrument uses a technique called sequential injection analysis and a new separation material—Sr-Spec resin [4,4'(5')-bis-(t-butylcyclohexano)-18-crown-6 in a polymeric resin], which was developed by E.P. Horwitz and coworkers at Argonne National Laboratory.

The production of nuclear weapons materials has generated large quantities of nuclear wastes that are currently stored in underground tanks at the Department of Energy's Hanford and Savannah River sites. A major fraction of the radioactivity in these wastes is given off by strontium-90, its daughter product yttrium-90, and cesium-137. These high-yield fission products with half-lives of approximately 30 years will continue to emit the majority of the radioactivity for the next several hundred years. In order to characterize the tank wastes and process them into stable forms for disposal, it is necessary to determine the concentrations of the radioactive isotopes.

The new instrument analyzes the strontium-90 concentration in 100-microliter samples (equivalent to one drop from a typical eyedropper) of waste solution. Operating under computer control, the strontium-90 in the sample is first purified on a sorbent extraction column and then analyzed on-line with a scintillation counter. The analytical results are obtained in approximately 30 minutes. In contrast, the traditional method of analyzing strontium-90

in tank wastes requires a tedious separation by multiple precipitation from fuming nitric acid, and the analytical results take from 10 to 30 days to obtain. This traditional method was still in use at Hanford in 1994. A more recent manual method implemented at PNL requires a day for a single sample, or 2 days for sets of 12 samples.

The new automated sequential injection analysis method has been used to measure strontium-90 concentrations in a variety of tank waste samples, and the results are in excellent agreement with results from the manual measurements. The advantages of the new strontium analyzer include faster analysis, greater precision and accuracy, reduced cost, reduced secondary waste, and improved worker safety.

Refinement of the technique and extension to the analysis of other radionuclides are currently ongoing. The Pacific Northwest Laboratory has submitted a proposal for FY 1996 funding to purchase equipment needed to implement the technique for routine analysis. In addition, the research team is investigating and developing new methods for using flow injection analysis for automatic measurement of actinides.

Publication

J. Grate, J. Janata, R. Strebin, O. Egorov, and J. Ruzicka. "Automated Analysis of Radionuclides in Nuclear Waste: Rapid Determination of Strontium-90 by Sequential Injection Analysis." *Analytical Chemistry* (accepted).

Radiochemical Analysis on a Microliter Scale Using Automated Sequential Injection Methods

- 100 microliter samples analyzed – small samples, reduced waste generation
- Radiochemicals separated on sorbent column – fast analysis (35 min. vs 2 days manually)
- Detection by on-line, flow-through scintillation counting – reduced labor and costs
- Fully automated using sequential injection – increased safety

Pacific Northwest Laboratory

Sequential Injection Analysis of Tank Waste Sample: Separation and Detection of Sr^{90} from SST938755

Pacific Northwest Laboratory

Quantification of Sr⁹⁰ in Tank Waste Samples

Pacific Northwest Laboratory

Evaluation of Cellular Response to Insult

Principal Investigators: C.G. Edmonds and R.F. Jostes

J.R. Strahler, University of Michigan, Ann Arbor; E. Mortz, Odense University, Denmark

Funding Source: Laboratory Directed Research and Development

Scientists at the Pacific Northwest Laboratory, working in collaboration with scientists at the University of Michigan, Ann Arbor, and Odense University, Denmark, are developing methods for the evaluation of cellular response to physical and/or chemical insult based on two-dimensional polyacrylamide gel electrophoresis (2D-PAGE) in combination with advanced mass spectrometric techniques. These efforts involve the exploitation of two distinct methodological approaches: 1) preparation of PAGE gel plugs by proteolytic enzymes for analysis by matrix-assisted laser desorption ionization (MALDI) time-of-flight mass spectrometry permitting the generation of peptide mapping data useful in searching appropriately formatted protein databases, and 2) analysis of PAGE preparations by electrospray ionization mass spectrometry (ESI-MS) and tandem mass spectrometry (MS/MS) permitting the generation of primary sequence information for unknown proteins. These new methods will permit the evaluation of the co-regulation of induced gene expression. The molecular details of induced cellular damage will reveal sensitive and specific markers of these events and provide important insight into the underlying scientific questions bearing on health effects of energy production and environmental contamination and remediation.

Mass spectrometric extensions of 2-D gel technology provide a strategy for the integration of protein and DNA sequence information in a comprehensive approach to the

study of cancer, differentiation and development, genetic variation, cellular response to stress, physical and/or chemical insult, and the diagnosis and treatment of genetic and clinical disease. The present emphasis on cDNA libraries as part of the Department of Energy Human Genome Project reflects an emphasis on sequencing the "functional" regions of the genome. The comparison with amino acid sequence enhanced 2-D gel protein databases for the intact cell and/or proteins generated by in vitro translation of the cDNAs would provide a critical link to the determined cDNA sequence. This would be the first step in defining the actual function of the sequenced genes.

Our developmental efforts have been closely coupled to applied collaborative studies in the Life Sciences Center concerned with the modulation of gene expression occasioned by physical and/or chemical insult. 2D-PAGE has shown differences in the pattern of gene products in extracts from the resistant melanoma cell line U1-mel exposed to low levels (50 to 500 cGy) of x-radiation which indicates the occurrence of enhanced or induced gene expression. In our initial effort using this biological system, we have pursued the hypothesis that such induced or enhanced gene products are observable by 2D-PAGE upon exposure to radon at radiation doses that are relevant to the question of the health effects of human radon exposure.

Two-dimensional electrophoretic separation of human melanoma nuclear proteins: Identification of altered protein expression following X-irradiation

JR Strahler, I Mortz, RF Jostes and CG Edmonds, Pacific Northwest Laboratory

Altered protein expression in human cells following radon exposure:

2D-PAGE separation of human melanoma extract

U1-Mel (suspension)
28 cGy
Silver staining

Mass spectrum of actin in 2-D gel plug

MALDI-MS

JR Strahler, I Mortz, RF Jostes and CG Edmonds
Pacific Northwest Laboratory

Functional Characterization of Megaplastids from Subsurface Bacteria

Principal Investigators: M.F. Romine, J.K. Fredrickson, J.D. Saffer, and L.C. Stillwell

Funding Source: Laboratory Directed Research and Development, Microbial Biotechnology Initiative

The objective of this research is to identify metabolic functions associated with large plasmids in the subsurface bacterium *Sphingomonas* F199 and related bacteria. It is known that numerous metabolic functions, such as metabolism of aromatic compounds, uptake of metals, metal resistance, and antibiotic resistance are encoded on large plasmids in other microorganisms. This suggested that megaplastids found in subsurface isolates might also harbor similar characteristics since approximately one-third of the bacteria isolated from the subsurface at the Savannah River Site in the OHER Subsurface Science Program have been shown to contain one or more large (> 100 kb) extrachromosomal genetic elements known as plasmids.

Previous investigations revealed that *Sphingomonas* F199 is capable of growing on toluene, naphthalene, dibenzothiophene, salicylate, benzoate, *p*-cresol, and all isomers of xylene. It was also found that four of the *Sphingomonas*-like strains from this site were capable of mineralizing toluene and naphthalene but that the ATCC strains 14666 (*Sphingomonas capsulata*) and 29837 (*Sphingomonas paucimobilis*) and subsurface strain B0477 were not. This suggests that most of the subsurface isolates are distinct from the known strains in their capacity to degrade aromatic contaminants. Further investigations revealed that F199 carries a plasmid of at least 100 kb that may account for the physiological difference between the subsurface isolates and the ATCC strains.

Research focus is on determining which aromatic catabolism genes are encoded on these large plasmids and on the relatedness between the different plasmids. The degree of similarity between the plasmids is being measured by restriction analysis and sizing of the plasmids and by probing with portions of F199 pNL1 and DNA encoding aromatic functions from unrelated bacteria.

Research findings for cosmid clones generated from the megaplastid, designated pNL1, indicate that one or two catechol-2,3 dioxygenase genes are plasmid encoded. The fact that the aromatic biodegradative genetic elements are commonly found as part of more extensive DNA coding regions in other bacteria, suggests that additional aromatic catabolic functions will also be found on pNL1.

The finding that catabolic functions responsible for contaminant destruction are found on plasmids isolated from the subsurface bacterium *Sphingomonas* is important because these organisms have been shown to metabolize a wide variety of aromatic compounds under conditions that could be exploited for in situ bioremediation and novel waste management processes.

Publications

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Duplication in Multimeric Enzymes

Compound C

Compound B

Compound A

Sphingomonas is able to "mix and match" enzyme subunits and so can utilize a broad array of aromatic substrates in the nutrient poor subsurface

Heterogeneous Atmospheric Chemistry: Molecular Dynamics Simulations of the Liquid/Vapor Interface of Water

Principal Investigators: R.S. Taylor, L.X. Dang, and B.C. Garrett

Funding Source: Laboratory Directed Research and Development

The earth's atmosphere is a multiphase mixture of gases, liquid cloud and precipitation droplets, solid ice crystals, and liquid and solid aerosols. Heterogeneous atmospheric processes, those processes that occur between two or more of these phases or that occur at the interface between two phases, have begun to gain recognition in atmospheric science over the last several years. For example, in the 1980s it was determined that the aqueous-phase oxidation of sulfur dioxide to sulfuric acid that occurs in cloud droplets accounts for 50 to 75% of the total sulfuric acid produced in the atmosphere from anthropogenic activities. The importance of heterogeneous processes in the atmosphere was further highlighted when reactions on the surface of ice crystals in polar stratospheric clouds were found to play a key role in the formation of the Antarctic ozone hole. Although heterogeneous processes play a major role in many important atmospheric chemical cycles, little theoretical or experimental work has been performed to understand these processes at a microscopic or molecular level.

One relatively simple, but extremely important, heterogeneous process is the uptake of a gaseous species by a liquid surface. There have been experimental efforts to determine the mass accommodation coefficient, a parameter that characterizes the uptake process, for a number of species over water. These experimental techniques currently cannot be extended to all species of interest (e.g.,

radicals). Furthermore, these techniques provide no direct information on molecular processes at the gas/liquid interface where the uptake occurs. In an effort to obtain a molecular-level understanding of the molecular uptake at aqueous interfaces, scientists in the Environmental Molecular Sciences Laboratory have undertaken a joint-theoretical-experimental-modeling investigation.

Molecular dynamics computer simulations have been used to explore the structural and dynamical properties of the liquid/vapor interface using the extended single-point-charge (SPC/E) model for the interaction energy between water molecules. The water configurations resulting from these simulations give a picture of an interface that is very rough on the molecular scale and one which changes rapidly on the time scale of picoseconds (10^{-12} seconds). As a test of the suitability of the SPC/E model for treating interfacial phenomena, the surface tension of water was calculated. The results of this test compare favorably with the corresponding experimental measurements. This work is currently being extended to the study of the interaction of adsorbate molecules with the aqueous interface. The direct calculation of the potential of mean force for inserting the adsorbate molecules into the liquid will allow the calculation of mass accommodation factor that are important in atmospheric modeling.

Snapshot of the gas-liquid interface of water and density profile as a function of distance perpendicular to the interface for a molecular dynamics simulation with 512 water molecules at a pressure of 1 ATM and temperature of 300K. The lighter shaded water molecules are those that are in regions where the average density is lower than 0.5 g/cc. Note that the simulations include two independent interfaces at $z \approx 25 \text{ \AA}$ and $50 \text{ \AA}$.

Computed surface tensions for the extended single-point-charge model of water compared with experimental values as a function of temperature.

Magnetic Resonance Spectroscopy Studies of Glasses, Minerals, and Catalysts

Principal Investigator: H. Cho

Funding Source: Laboratory Directed Research and Development

The elucidation of the link between structure, dynamics, and macroscopic properties of inorganic materials is the focus of this project. The inorganic materials we have chosen to study mainly include metal-supported catalysts, multicomponent glasses, and natural and synthetic minerals that arise in connection with Hanford remediation science issues. Spectroscopy, primarily magnetic resonance and infrared, combined with a host of analytical techniques, such as ICP, thermal analyses, and x-ray crystallography, are the principal methods we have used to probe these samples.

The lack of atomic-level information on certain metal-supported catalysts, multicomponent oxide glasses, and oxide minerals is a significant impediment to informed decision making on waste treatment and storage strategies at the Hanford Site. The first category of materials, metal-supported catalysts, form the basis of an attractive scheme to treat organic wastes at the Hanford Site. Their potential usefulness is suggested by the finding that some of these catalysts promote the decomposition of common Hanford wastes—halogenated hydrocarbons—into relatively benign products. The second category of materials, multicomponent oxide glasses, is crucial in a technology—vitrification—that is actively being developed at Hanford as a method to store radioactive and chemical wastes for extended periods. Waste streams at Hanford create unique problems for vitrification technologies that necessitate a greater understanding of glass-forming materials before specific glass compositions and synthetic methods can be confidently proposed. Finally, important ecological issues concerning the effects of wastes and storage technologies on the environment reduce to questions of mineralogy, and the interactions of minerals with organic liquids, heavy metals, radioactive isotopes, and water. Water and ionizing radiation especially are known to have profound consequences on the physical and chemical properties of minerals even at low concentrations.

The materials described above share similarities from a spectroscopic and analytical perspective that have enabled us to apply a unified, common approach on most of these

samples. Solid-state magnetic resonance spectroscopy, coupled with infrared spectroscopy, form the core of the methods that are employed in this study. Aluminum-27, phosphorus-31, and silicon-29 nuclear magnetic resonance (NMR) experiments have produced data that have been used to identify aluminum, phosphorus, and silicon species and environments in catalysts, glasses, and minerals, thus elucidating the major structural components in many of these systems. A relatively novel and untried aspect of the magnetic resonance portion of this work is application of hydrogen NMR, both proton and deuterium, to uncover the forms of hydrous species in nominally anhydrous substances such as the minerals and oxide glasses. The poor resolution of solid-state proton NMR spectra typically precludes useful interpretation, but through a combination of variable temperature relaxation studies, resolution enhancement techniques such as CRAMPS, and synthetic strategies such as isotopic dilution, coupled with available analytical technologies, this problem is potentially surmountable. Similar techniques are being used to probe organic molecules and water adsorbed to the surface of catalyst materials. The results of the spectroscopic methods, together with common and accessible analytical tools such as x-ray diffraction, polarized optical microscopy, and thermal gravimetric analysis, provide a way of obtaining a comprehensive and informative picture of host-guest interactions in these materials.

Future work will consist of a continuation of the spectroscopic studies and an increased effort in synthesis of model glass, mineral, and catalyst compounds for comparison with the focus samples.

Publications

J.M. Koons, E. Hughes, H.M. Cho, and P.D. Ellis. 1995. *J. Magn. Reson. A* 114, 12.

H. Cho. *J. Magn. Reson. A* (submitted).

Microbial Genome Research

Principal Investigator: J.D. Saffer

Funding Source: Laboratory Directed Research and Development

The identification of genes in novel bacteria is important for devising bioremediation strategies. However, finding important genes in these bacteria often cannot be accomplished by traditional methods since genetic tools and a description of the biochemical pathways are unavailable. To circumvent these shortcomings, genomic research methods have been applied to find and characterize genes of importance. Using methods developed at Pacific Northwest Laboratory, researchers have isolated a megaplasmid, a large accessory genetic element, from a deep subsurface bacterium, called F199. Through a combination of physical mapping, biochemical analyses, and DNA sequencing, scientists identified several genes on the megaplasmid that encode enzymes involved in degrading aromatic hydrocarbons.

A subsurface organism, strain F199, isolated from sediments 407 meters below the soil surface at DOE's Savannah River Site, has the ability to use toluene, all xylene isomers, *p*-cresol, naphthalene, salicylate, and benzoate as sole carbon and energy sources. This isolate has been classified in the genus *Sphingomonas* based on 16S rRNA gene sequence and fatty acid analysis.

Members of the genus *Sphingomonas* are known to have extensive abilities to degrade xenobiotic compounds, but little is known about the genes involved or their organization. Of special interest is an understanding of the

genetics of subsurface bacteria, which may be particularly important for bioremediation. This PNL research provides the first linkage of a catabolic function to a plasmid in the genus *Sphingomonas*.

Additional genetic and biochemical analysis of F199 and the pNL1 plasmid will provide important insights into the nature of aromatic degradation genes from the isolated deep subsurface environment. In addition to aromatic degrading ability, F199 is capable of catabolizing halogenated compounds. Identification of the pathways involved will have broad application. In the longer term, integration of this work with PNL's other ongoing bioremediation efforts within the Microbial Biotechnology Initiative including research in fundamental microbiology, bacterial enzymology, bioprocessing, and technology analysis will provide a foundation for PNL's future broader participation in biotechnology and biomolecular research.

Publication

L.C. Stillwell, R.P. Schneider, S.J. Thurston, M.F. Romine, J.K. Fredrickson, and J.D. Saffer. 1995. "Physical Mapping and Characterization of a Catabolic Plasmid from the Deep Subsurface Bacterium *Sphingomonas* sp. F199." *J Bacteriol* 177:4537-4539.

Biology & Chemistry Department
Pacific Northwest Laboratory

Using Genome Research to Identify Genes of Importance

Using genome research methods, PNL scientists are identifying bacterial genes of environmental, energy, and industrial importance. DNA is isolated and the individual genetic elements characterized. A physical map of the relevant DNA is prepared along with a "library" of separate regions of that DNA. These tools can be used to identify the genes of interest, for which the DNA sequence is determined. This information can then be applied to problems in bioprocessing, bioremediation, and environmental monitoring.

Biology & Chemistry Department
Pacific Northwest Laboratory

Localization of Aromatic Degradation Genes on the Megaplasmid, pNL1

A 180 Kb megaplasmid was isolated from the deep subsurface *Sphingomonas* bacterium F199. Using genome research methods, a physical map was prepared, which indicates the relative positions where molecular scissors called restriction enzymes recognize specific DNA sequences. This physical map was one of the tools used to identify the location of two key enzymes, *bphC* and *xylE*, for the degradation of aromatic hydrocarbons.

Nuclear Magnetic Resonance Investigations of the Early Stages of Biomineralization

Principal Investigators: P.D. Ellis and R.A. Wind

Funding Source: Laboratory Directed Research and Development

This research aims to examine the mineralization process and determine the course of events that lead to the formation of mature bone in the body. We have used a system developed by Dr. Roy Wuthier at the University of South Carolina involving matrix vesicles incubated in synthetic cartilage lymph solutions (SCL). Since matrix vesicles are the sites of initial calcification in the body, this has allowed us to study the phases present at very early stages of mineralization. The figure shows the ^{31}P NMR spectra obtained from matrix vesicle samples incubated for varying time periods in the SCL solution. The spectra after the initial time interval are mainly apatitic in nature but a computer analysis of the spectra using factor analysis shows that there are three phases present in the vesicles. We have identified these phases, in order of concentration as hydroxyapatite, amorphous calcium-phosphate, and a phosphatidylserine calcium-phosphate complex.

Investigations into the biomineralization process are important for a variety of reasons. The series of events that leads to the formation of mature bone is not fully understood and many questions arise concerning the phases that are present particularly at the earliest stages of biomineralization. A more extensive knowledge of the way bone forms will aid our understanding of how certain diseases of the skeletal system occur and may help in

the search for osteoporosis and osteoarthritis. This knowledge will also help in the manufacture of more natural bone implants and prosthetic limbs.

Future work in this area will involve the examination of how the early mineral phases respond to the damaging effects of radiation and chemicals. The matrix vesicles will be subjected to various toxins and the mineral examined by NMR techniques.

Publications

B.A. Concannon, B.R. Genge, J.M. Koons, P.D. Ellis, R.A. Wind, and R.E. Wuthier. "NMR investigations on the mineral formed in matrix vesicles." (in preparation).

B.A. Concannon, B.R. Genge, J.M. Koons, P.D. Ellis, R.A. Wind, and R.E. Wuthier. "Structural studies on the mineral formed during induction of mineralization in matrix vesicles." (in preparation).

B.A. Concannon, L. Wu, P.D. Ellis, R.E. Wuthier and B.R. Genge. "Phosphatidylserine calcium-phosphate and its involvement in the mineralization process." (in preparation).

Macromolecular Structure and Dynamics

- These spectra show the growth of mineral in the matrix vesicles.
- Vesicles are incubated for varying periods of time in a solution closely resembling the extracellular fluid around mineralizing tissue.
- The mineral present after 4 hours is mainly apatitic in nature.
- The chemical shift of the phosphate is very similar to that of hydroxyapatite.
- The 0 hour sample is very different and has large chemical shift anisotropy indicative of a protonated phosphate environment.
- Factor Analysis of the spectra have shown the presence of three components in each mineral sample.

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Macromolecular Structure and Dynamics

- The components have been identified as hydroxyapatite, amorphous calcium-phosphate and a phosphatidylserine calcium-phosphate complex.
- It is also possible to analyze the evolution of each of the three phases with time.
- Hydroxyapatite grows, amorphous calcium-phosphate initially grows and then lessens and the phosphatidylserine calcium-phosphate complex present at higher concentrations at the beginning dies away.

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Macromolecular Structure and Dynamics

Cross Polarization Spectra of Mineral Samples.

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Macromolecular Structure and Dynamics

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Nuclear Magnetic Resonance Studies of Altered DNA/Protein Interactions

Principal Investigator: M.A. Kennedy

Funding Source: Laboratory Directed Research and Development

We have recently identified a new structural element in DNA. Unusually large amplitude and slow conformational dynamics had been previously noticed at TpA step in a single sequence context. Our recent studies show that this phenomenon occurs at all TpA steps in DNA and can be detected by nuclear magnetic resonance experiments. The NMR-derived structure shows that the TpA site is characterized by poor base stacking interactions that lead to highly dynamic and localized regions in DNA which may be important for understanding protein interactions localized at TpA steps, such as the trp promoter, several restriction enzymes sites, and the TATA binding protein promoter site.

DNA structure is of interest to us because of our emerging research in the area of DNA repair. Our goals are to elucidate the structural basis for protein recognition of DNA damage and the subsequent signaling steps in this process. Part of this understanding will be derived from an analysis of how DNA structure is affected by DNA damage and how this structure is further modified upon binding by a repair protein. Understanding the process of DNA repair could have consequences for understanding the associated health risks related to exposure of residual contaminants during or after cleanup activities at Department of Energy sites. Our future directions will focus on determining the structure of damaged DNA molecules and the proteins that recognize or bind to damaged DNA. Ultimately, we expect to provide the most complete picture of the recognition process by determining the structure of complexes between the repair protein and damaged DNA.

Publications

M.A. Kennedy, M.A. Lingbeck, B.D. Thrall, K. McAteer, M.G. Kubinec, K.B. Geahigan, B.R. Reid, D.S. Springer, and G.P. Drobny. "Understanding Patterns of Benzo[a]Pyrene Diol Epoxide Adduction in Poly:G DNA Regions." (in preparation).

M.A. Kennedy, M.G. Kubinec, J.M. Lingbeck, K. McAteer, B.D. Thrall, and P.D. Ellis. "750 MHz NMR Studies of Chemically Modified DNA Structure/Dynamics: Sequence Context Effects and Protein Recognition." *Bull. Magn. Res.* (in press).

J.M. Lingbeck, M.G. Kubinec, J. Miller, B.R. Reid, G.P. Drobny, and M.A. Kennedy. "Effect of Adenine Methylation on the Structure and Dynamics of TpA Steps in DNA: NMR Structure Determination of [d(CGAGGTTTAAACCTCG)₂] and Its A9-Methylated Derivative at 750 MHz." *Biochemistry* (submitted).

K. McAteer, P.D. Ellis, and M.A. Kennedy. "NMR Evidence for Base Dynamics at All TpA Steps in DNA." *J. Am. Chem. Soc.* (submitted).

K. McAteer, P.D. Ellis, and M.A. Kennedy. "The Effects of Sequence Context on Base Dynamics at TpA Steps in DNA Studied By NMR." *Nucleic Acids Res.* (in press).

750 MHz ^1H NMR spectrum of CGAGGTTTAAACCTCG shown in the aromatic proton region. Although chemically identical, the H2 resonances of the four adenines in the sequence have strikingly different linewidths. This is due to sequence-dependent base dynamics which occurs at TpA steps in DNA.

A Physically Based Mountain Watershed Model Driven by a Regional Climate Model

Principal Investigators: L.R. Leung, M.S. Wigmosta, S.J. Ghan, D.J. Epstein, and L.W. Vail

Funding Source: Laboratory Directed Research and Development

One of the more serious potential consequences of a global greenhouse warming is a change in the phase of wintertime precipitation in temperate regions. Even if the amount of precipitation does not change, the expected higher proportion of precipitation falling as rain rather than snow in a warmer climate has serious implications for management of water resources. In the western United States, where about 70% of the annual runoff is derived from snowmelt in headwater catchments, a higher fraction of wintertime precipitation falling as rain implies reduced storage of water in the winter snowpack and hence (unless additional artificial reservoirs are constructed) a higher likelihood of both wintertime flooding and diminished water resources during summer. Because these impacts could lie well beyond the range of recorded history, physically based models are needed to estimate the impact of greenhouse warming on water resources in mountainous regions.

We have developed a coupled watershed/meteorology model system that meets these needs. It consists of a physically based watershed model that treats surface hydrologic processes at 90-meters resolution, driven by meteorology simulated by the Pacific Northwest Laboratory regional climate model, which features a novel subgrid orographic precipitation scheme. The figure illustrates how the subgrid scheme is applied to the Middle Fork Flathead watershed in Montana to yield a high resolution estimate of precipitation.

To demonstrate the value of driving the PNL watershed model with meteorology simulated by the PNL regional climate model, we have performed two 12-month watershed simulations for the Middle Fork Flathead River

basin. In one simulation the watershed model is driven by meteorology derived from station observations within the watershed, the other by meteorology simulated by the PNL regional climate model. We have found that the discharge rate simulated when the watershed model is driven by the simulated meteorology is comparable if not superior to that simulated with observed meteorology. This success suggests that the physically based watershed/regional modeling system can be applied to numerical climate change experiments. The regional climate model can be driven by meteorology simulated by a global climate model under elevated greenhouse gas concentrations. The watershed model can be applied independently to any number of watersheds, and discharge from each outlet can be routed by a river flow routing model. In this manner, it should be possible to model the impact of greenhouse warming on entire river systems.

Publications

L.R. Leung and S.J. Ghan. "A Subgrid Parameterization of Orographic Precipitation." *Theoretical and Applied Climatology* (in press).

L.R. Leung, M.S. Wigmosta, S.J. Ghan, D.J. Epstein, and L.W. Vail. "Application of a Subgrid Orographic Precipitation/Surface Hydrology Scheme to a Mountain Watershed." *J. Geophys. Res.* (accepted).

M.S. Wigmosta, L.W. Vail, and D.P. Lettenmaier. 1994. "A Distributed Hydrology-Vegetation Model for Complex Terrain." *Water Resources Res.* 30, 1665-1679.

Subgrid Orographic Precipitation Scheme At the Middle Fork Flathead Watershed

Subgrid orographic precipitation scheme. Upper left: Surface elevation from digital elevation model for the Middle Fork Flathead watershed in Montana. Upper right: frequency distribution of surface elevation classes within the watershed. Lower right: annual mean of precipitation simulated for each surface elevation class. Lower left: mapping of simulated precipitation to the watershed.

Rovibrational Analysis of Chlorine Nitrate

Principal Investigators: T.A. Blake, S. Xu, and S.W. Sharpe

Funding Source: Atmospheric Radiation Measurement Program, Global Climate Change Initiative, and Laboratory Directed Research and Development

Chlorine nitrate is an important reservoir species in stratospheric chemistry: it sequesters the reactive molecules ClO and NO₂, both of which participate in catalytic cycles that destroy stratospheric ozone. Ozone degradation proceeds via a catalytic process involving atomic chlorine, which can be produced by the photodissociation of freons (e.g., CF₂Cl₂). Chlorine nitrate has been postulated to act as a reservoir for atomic chlorine and may be important in terminating this catalytic cycle.

Monitoring the chlorine budget of the stratosphere has become an important goal of atmospheric scientists. Chlorine nitrate has been detected by ground-based and balloon-borne infrared spectrometers and by an infrared emission spectrometer on board the Upper Atmospheric Research Satellite. Reducing the data from these instruments to determine the concentration of chlorine nitrate has been, however, problematic. The ν_4 fundamental band in the vicinity of 780 cm⁻¹ is typically used for the atmospheric detection of chlorine nitrate because it is of moderate intensity and it is unobscured by strong absorptions from other molecules. Uncertainties in the absolute absorption cross section and the spectroscopic constants of the excited vibrational state have led to systematic errors as large as 50% in the concentration measurements of this molecule. Laboratory measurements of this band have encountered two difficulties: 1) chlorine nitrate is an unstable molecule that decomposes to ClO and NO₂ when in contact with glass or metal components; and 2) the molecule has an extremely congested rovibrational spectrum due to its small rotational constants, the ³⁵Cl and ³⁷Cl isotopic species whose bands lie within 2 cm⁻¹ of one another, and hot bands that have significant population

even at stratospheric temperatures of 195 K. Previously reported infrared spectra of ClONO₂ are not of sufficiently high resolution and/or quality to allow for an unambiguous rovibrational assignment of the observed transitions.

For the development of rapid, reliable techniques for identifying and quantifying ClONO₂, an infrared "road map" and accurate upper-state molecular constants are needed. We have obtained such spectra by seeding chlorine nitrate in a pulsed jet of argon, thus obtaining the rotationally resolved spectrum of the fundamental band using tunable infrared diode lasers. The near-perpendicular crossing of the laser and molecular beam yields sub-Doppler resolution, which, combined with a jet rotational temperature of approximately 7 K, gives a rotationally resolved and greatly simplified spectrum of the *P* and *R* branches of both the ³⁵Cl and ³⁷Cl isotopomers. Over 1250 transitions were measured, assigned, and fit to a model Hamiltonian to provide spectroscopic constants with megahertz precision for the excited state of the band. Careful measurements were also made of the intensities of several transitions to give an estimate of the vibrational transition moments for the planar molecule. Subsequent calculations have provided absorption cross sections for individual transitions throughout the band.

Publication

S. Xu, T.A. Blake, and S.W. Sharpe. "High-Resolution Infrared Spectroscopy of the ν_4 Fundamental Band of Chlorine Nitrate." *J. Mol. Spectrosc.* (submitted).

ROVIBRATIONAL ANALYSIS OF CHLORINE NITRATE

- An important reservoir species in stratospheric chemistry: active in catalytic cycles that destroy stratospheric ozone.
- Monitored using ν_4 band at $780\text{-}1$ in mid-infrared.
 - large uncertainties in absorption cross section yield systematic errors as large as 50%
- High-resolution spectra obtained at PNL provide
 - accurate "road map" of absorption features, with quantum assignments
 - precise molecular constants
 - accurate absorption cross sections for individual transitions

Chlorine Nitrate

CS&D/EMSL

The Spatial Distribution of Damage Sites in DNA

Principal Investigator: M.K. Bowman

Funding Source: Laboratory Directed Research and Development

The spatial distribution of damage in DNA produced by ionizing radiation using a new method was demonstrated at Pacific Northwest Laboratory. A Fourier Transform Electron Paramagnetic Resonance technique was used to measure distances between sites on the DNA. Isolated DNA was cooled to liquid nitrogen temperatures and irradiated with ionizing radiation. The cold temperature froze in the initial damage species known as free radicals. The ionizing radiation produces small clusters of damage with a diameter of 5 to 10 nanometers. The data also show that at low doses of radiation, the damage is distributed nonuniformly in space as hypothesized by the Locally Multiply Damaged Site model, but that at very large doses, the regions of damage begin to overlap.

DNA is the repository for the genetic information necessary for human life. Thus, protecting and regulating the DNA in the cell is a critical activity that involves huge complexes of many different proteins. It is extremely difficult, if not impossible, to determine the structure of many of these protein complexes that guard and control the DNA because of their size. This prevents a molecular, mechanistic understanding of how the cell functions and how DNA is controlled, regulated, and protected. The ability to measure physical distances in the range covering the size of large DNA-protein complexes using Fourier Transform Electron Paramagnetic Resonance now provides a new method for answering mechanistic and structural questions that will help us understand and predict the response of living cells to radiation, chemicals and drugs.

The Department of Energy is facing challenges from chemical and radiological waste resulting from decades of weapons and energy production activities. A major portion of that challenge arises from the potential long-term human impact of those wastes. The wide range of types of waste and potential exposure levels requires the ability to predict human response based on how humans and their DNA react to molecular insults. This work provides a new method for obtaining the molecular information necessary to predict the impact of waste on DNA in the cell.

This work will continue as part of research to determine the structure of the nucleotide excision repair process in a proposal about to be submitted to DOE/OHER. The nucleotide excision repair process is a major mechanism used by human cells to correct damage to the DNA caused by radiation or chemical insult. The work makes use of free radical labels that will be attached to specific locations in DNA or proteins. The distances between pairs of labels and the DNA-protein complex will be measured. Changes in those distances as the proteins carry out their function will be integrated with other structural and mechanistic information to determine both the molecular-resolution structure and the functional mechanisms involved in nucleotide excision repair.

Effect of Hydration on Cluster Size

Surface Studies of Silver Alumina Systems by Solid-State Nuclear Magnetic Resonance and Infrared Spectroscopy

Principal Investigator: P.D. Ellis

Funding Source: Laboratory Directed Research and Development

The promoter effects of alkali metals in silver alumina systems have been studied by low temperature solid-state NMR. The investigation focused on measuring the inter-nuclear carbon-carbon bond distance of ethylene adsorbed on the surface of such systems as a function of cesium loading. It was shown that the bond distance increased as the cesium loading increased. Furthermore, by using a technique called spin echo double resonance (SEDOR) the proximity of the cesium to the ethylene molecules was probed and it was found that in this investigation the cesium and ethylene molecules were within 4 Å of each other. These experiments demonstrate that the promotion by cesium salts is a local phenomena on the silver surface. Hence, the efficiency of the promoter could be based on its ability to act to mitigate the surface dipole or work function. Further work in the area of poisons (i.e., those reagents that would enhance the surface dipole, anions, or anions with protons, such as, hydrogen phosphate) needs to be done. From such work one could deduce an optimum anion for the cesium cation.

It has been proposed that such silver alumina systems may have value as catalysts for the dehalogenation of environmental contaminants such as carbon tetrachloride and dichlorobenzene. Using infrared spectroscopy, analysis of the gaseous products from passing carbon tetrachloride over a variety of silver/alumina and alumina only systems with different carrier gases has been performed. The principal reaction products that have been identified were methane, hydrochloric acid, carbon dioxide, and carbon monoxide. The results from using different supports indicate that there are two reactions occurring. The first, which occurs only in the presence of hydrogen and on a silver alumina system, is the production of methane together with hydrochloric acid. The second is a reaction that occurs at the alumina surface where carbon tetrachloride reacts to form carbon dioxide and hydrochloric acid and is independent of carrier gas. To date, our analysis of catalytic destruction of CCl_4 is quantitative. Hence, this appears to be a viable method for the destruction of halogenated hydrocarbons. That is the future direction of our proposed research.

Macromolecular Structure and Dynamics

- SEDOR Experiment indicates the cesium and ethylene are in a proximity of approximately 4 Angstroms.
- Spin Echo Experiment shows that with increasing cesium concentration the strength of the carbon-carbon double bond is decreasing. Bond length increased by 0.026 of an Angstrom going from an unpromoted catalyst to one containing 26% w/w cesium.

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Results of SEDOR Experiment

Macromolecular Structure and Dynamics

Spin Echo Results

Environmental Molecular Sciences Laboratory

System for Modeling Climate Change Impacts on U.S. Water Resources

Principal Investigators: D. Epstein and N. Rosenberg
R. Srinivasan, Texas A&M University

Funding Source: Office of Health and Environmental Research, Electric Power Research Institute, U.S. Environmental Protection Agency, Laboratory Directed Research and Development

Scientists at Pacific Northwest Laboratory, in cooperation with Texas A&M University, have adapted the Hydrologic Unit Model for the United States (HUMUS) to the needs of an integrated assessment of climate change impacts on the United States. HUMUS was originally developed by Texas A&M for the Soil Conservation Service which is required to report to Congress every 10 years on the state of natural resources in the country. HUMUS applies a physically based, distributed hydrologic model to about 40,000 small basins for the conterminous U.S. The level of detail required by the Soil Conservation Service is feasible for an analysis done once each decade to describe current conditions. It is impractical, however, for the purposes of climate change analysis where numerous climate, land-cover, and technology scenarios must be examined.

We have modified HUMUS so that each of the 2101 U.S. Geological Survey's eight-digit basins (average size about 5000 square kilometers) is treated as uniform in soil, land cover, and climate. Outputs of general circulation models that predict the regional distribution of climatic change in response to emissions of greenhouse gases are used as forcing in the modified HUMUS to simulate the resulting process hydrology. Estimates of such variables as evaporation, runoff, water yield, and groundwater recharge for each of the eight-digit basins can be provided. Flows can be routed from each basin to the next downstream basin, so that water availability can be estimated at any point or points of interest.

Results of preliminary HUMUS runs have been compared with other estimates of water yield across the United States with generally good results. Adjustments have been needed for the mountainous regions of the country because of difficulties in adequately describing climate in larger areas of complex terrain with a single point. In addition, better parameterizations in isolated eight-digit basins such as in the lake region of Minnesota and in southwestern deserts are required.

Data produced by PNL's modified HUMUS are used in conjunction with models of the climate sensitivity of agriculture, forestry, and unmanaged ecosystems as part of the Global Change Assessment Model (GCAM). GCAM is an integrated assessment tool that links physical, social, and economic information to assist agencies, governments, international bodies, and the private sector in understanding possible consequences of and response to global change.

Currently, HUMUS and the other GCAM simulation models are being extended to the rest of North America by a consortium of natural resource modelers from Canada and Mexico organized by PNL under the Laboratory Directed Research and Development-funded North American Energy, Environment and Economy (NA3E) program. NA3E has prepared a number of proposals for support by outside agencies. The first of these, a proposal to study the sensitivity of North American agriculture to El Nino driven climate variability, has been funded by the National Aeronautics and Space Administration.

Simulation base
Datatype yld
Timeunit ann

Calibration run of HUMUS-simulated water yield under the current climate

Simulation giss-t5.0-c750

Datatype yld

Timeunit ann

Water yield under a climate change scenario produced by the Goddard Institute for Space Studies

Simulation giss-t5.0-c750
Datatype Percent Change yld
Timeunit ann

Percent difference in available water between the two simulations

Tumor Formation in Cells and Tissues Studied by Means of Liquid-State and Solid-State Nuclear Magnetic Resonance

Principal Investigator: R.A. Wind

Funding Source: Laboratory Directed Research and Development

A nuclear magnetic resonance (NMR) study has been undertaken of R3230AC rat mammary carcinoma, originally induced by dimethylbenzanthracene, and for this investigation obtained after transplantation of tumor cells in female Fischer rats. Both ^1H and ^{13}C liquid-state and ^{13}C high-resolution solid-state NMR has been used, the latter on frozen samples at -40 and -100°C . Compared with the results obtained on normal rat mammary epithelial cells, in the solid-state experiments the lipid composition was found to be different in the tumor sample, and an increased mobility of part of the lipids was observed in the tumors. The latter result was confirmed by the liquids NMR experiments. Hence both methods can be used for discriminating between healthy and malignant cells, and as such might be useful for cancer diagnosis.

Current investigations at Pacific Northwest Laboratory are extending the cancer research from whole animal systems to the cell and tissue level. A better understanding of toxic insult and response and repair requires an extension of the current animal investigations to a progressively sharper focus on tissue, cellular, and ultimately molecular events. The goal of this project is to study the changes in the structures and dynamics between normal and tumorous cells and tissues after exposure on a molecular level.

Liquid-state NMR spectroscopy is extensively used to characterize tumors in a noninvasive, nondestructive manner in cells and tissues obtained from animals and humans. In the proposed study the capabilities of NMR in cancer research will be extended by performing multi-nuclear liquid-state NMR in large external fields, and by performing multi-nuclear solid-state high-resolution NMR on frozen samples. Whereas in liquid-state NMR mainly mobile compounds are observed; in solid-state NMR large cell constituents can be studied which are not accessible

with solution NMR, long-term studies can be performed without degrading the samples, and slow molecular motions can be examined which are normally masked by the rapid overall molecular tumblings. As such, both techniques can be regarded as complementary, and the first results indicate that this is indeed the case.

The research will result in several deliverables: partially unique capabilities at PNL for cancer research, an improved understanding of the mechanisms involved in the carcinogenic process, contributions in the areas of risk assessment and environment-related health research, such as the evaluation and improvement of alternate multistage risk assessment models, and medical spin-offs, such as an improved differentiation between precancerous and cancerous lesions, and an improved evaluation of treatment response.

Future directions of the research include a similar investigation on mammary preneoplastic lesions, and the evaluation of spectral editing techniques in order to measure the NMR spectra of the various macromolecular and molecular compounds in intact cells and tissues.

Publications

R.A. Wind, B.A. Concannon, K.M. Groch, D.N. Rommereim, and R.A. Santos. "An Investigation of Rat Mammary Healthy and R3230AC Tumor Tissue and Cells with Solid State ^{13}C NMR." *Solid State Nuclear Magnetic Resonance* (submitted).

R.A. Wind, B.A. Concannon, K.M. Groch, D.N. Rommereim, and R.A. Santos. "A ^1H and ^{13}C solution NMR study of Rat Mammary Healthy and R3230AC Tumor Tissue and Cells." (in preparation).

Solid State ^{13}C NMR Spectra of Rat Mammary Cells and R3230AC Tumors

- The various intensities in the spectra are mainly due to the cell proteins (both in the membranes and the cytoplasm) and the membrane lipids. The difference spectrum indicates that the lipid composition and perhaps the protein composition are different in the normal and malignant cells. This research is part of an on-going investigation by means of *in vivo* and *in vitro* Magnetic Resonance Spectroscopy and Imaging of the molecular changes in cells and tissues during carcinogenesis resulting from exposure to toxic chemicals.

Solid State ^{13}C NMR Spectra of Rat Mammary Cells and R3230AC Tumors

Environmental Molecular Sciences Laboratory

Two Catalytic Lewis Acid Sites Identified on Modified Alumina Surfaces

Principal Investigators: M.K. Bowman and S.A. Dikanov

R.I. Samoilova, Institute of Chemical Kinetics and Combustion, Russian Academy of Science

Funding: Laboratory Directed Research and Development and Special American Business Internship Training Program

Scientists working in the Environmental Molecular Sciences Laboratory at the Pacific Northwest Laboratory have succeeded in identifying at least two types of Lewis Acid sites on the surface of alumina catalysts using Fourier transform electron paramagnetic resonance spectroscopy. These two types differ in the manner in which they bind reacting molecules: one type holds the molecules at one end while the other utilizes two surface aluminum atoms to hold both ends of the molecule. Modification of the alumina surfaces with either phosphoric or boric acid, which changes the selectivity, reactivity, and useful lifetime of the alumina catalysts, also changes the relative amounts of these two types of sites. In this way, the structure of the catalytically active sites can be related to their reactive properties, revealing ways of improving performance of catalysts.

Alumina has the ability to catalyze a wide range of chemical reactions because of the wide range of surface sites that are found on it. In many applications, alumina suffers from being too reactive: selectivity is poor because alumina catalyzes more than the desired reaction, and the useable lifetime is poor because extremely reactive sites produce coke which quickly covers the entire surface, killing the catalyst. Chemical modification of the alumina surfaces is becoming a popular method of lowering the reactivity of alumina while prolonging lifetime and improving its selectivity as a catalyst. Finding a chemical

modification that is effective is largely a matter of trial and error because the nature of both the desired surface sites and the deleterious sites are largely unknown. This work is one of the few methods for characterizing those sites and establishing some of the understanding necessary to allow the rational design of catalysts.

Alumina-based catalysts are utilized extensively throughout the petrochemical industry to transform one type of molecule into another more desirable type. The production of virtually all gasoline and plastics is based on the use of catalysts. Thus, even a small improvement in the performance of catalysts can have a substantial impact on both national economic competitiveness and on the national energy supplies.

This work will continue as part of research to understand the catalytic properties of alumina in a proposal submitted to DOE/BES. The work makes use of reporter molecules formed at catalytically active sites to obtain structural and mechanistic information about those catalytically active sites. Progressive chemical modification of the alumina surface will be used to correlate the reactivity with its structure with the goal of understanding structure/function relationships on alumina and of developing strategies for rational control of catalytic properties through chemical modification of the surface.

HYSCORE EPR of Surface Modified Alumina

Spectrum of reporter groups on an alumina surface showing peaks from reporter groups at different types of catalytically active sites.

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