Research

Environmental & Water Studies

The Environmental and Water Studies Program encompasses both teaching and research. The research program emphasizes several major areas of activity and, as a general philosophy, promotes interdisciplinary projects. Laboratory research is generally conducted within the Environmental Fluid Mechanics Laboratory and the Water Quality Control Laboratory. Often faculty, staff and students from several specialty areas work as a team on a given research endeavor. Student participation is a vital element; at any one time, approximately forty graduate students, representing all levels of degree candidacy, are contributing to one or another of the approximately twenty-five funded research projects. The size and diversity of the research program provide numerous learning opportunities outside the classroom, and stimulate a level of excitement for learning through research that is rare. Student-faculty relations are relaxed and friendly. Student initiative is encouraged in conceiving and conducting research, as well as in communicating results. Current research includes laboratory and field studies on the movement and fate of organic and inorganic compounds in ground water and surface waters; physical, chemical, and biological processes and mechanisms responsible for the release, transport, transformation, and retention of contaminants; contaminant control processes (especially the removal of trace contaminants); mathematical modeling of important processes as well as hydrologic phenomena; stochastic modeling of spatial variability and uncertainty in ground water flow and transport; the development of alternative energy sources; fundamental principles of physical, chemical and biological treatment technologies for water, waste water and solid wastes. In the environmental fluid mechanics area current research is

focused on stratified flows in lakes and reservoirs, natural and forced convection flows in energy systems, energy and mass transfer across the ocean-atmosphere interface, and simulation of mesoscale phenomena in the oceans and surface layers of the atmosphere. Other research includes hydrologic modeling, interaction between surface water and ground water, and a comprehensive program on the fundamentals of fluid transport, including turbulence and mixing in natural water bodies and the mechanism of dispersion in porous media flows. In the environmental planning and management area current research is focused on implementation of environmental policies and programs in developing countries and on the applications of expert systems in operating water resources systems. The following is a list of currently active externally funded research projects:

Environmental Fluid Mechanics

- An Experiment to Measure the Mixing Efficiency and Fine-Scale Structure in a Breaking Internal Wave - Koseff, J.R. and Troy, C. (NSF) We are studying an internal-wave breaking event in the laboratory with the purpose of (i) measuring the mixing efficiency of the breaking and the resulting turbulence, and (ii) characterizing the finescale physical processes associated with the breaking. We choose to focus on a breaking internal wave at a density interface because of the documented importance of this phenomenon in producing turbulence in the ocean interior in general, and at the thermocline in particular. In general, much more is known about the energetics of the mixing produced by shoaling internal waves than that produced by breaking internal waves away from boundaries. We perform the experiment by creating a wave-breaking event at the interface of a two-layer stratified system (using salt as the stratifying medium) in a laboratory facility of dimension 4.8m long by 0.3m wide by 0.6m deep. The wave signal is created using a modified version of the "chirp" process as first proposed by Rapp and Melville (1990). Using this technique we focus the energy of an internal wave group, generated by a wavemaker located at the density interface, at a specified location in the tank: the focal point being the location of the wave breaking event.

  We expect to run three sets of experiments. In the first and second sets we will concentrate on visualizing the breaking process over a range of stratification conditions, and on measuring the mixing efficiency of the breaking internal wave.

  In the third set of experiments we will use Digital Particle Velocimetry (DPTV) and Laser Induced Fluorescence (LIF) techniques to study the physics and finescale structure of the breaking event and the turbulence created by the breaking wave.

- The Hydrodynamics of Phytoplankton Removal in Benthic Boundary Layers by Suspension - Feeding Bivalves - Monismith, S. G. and Koseff, J. R. (National Science Foundation (NSF)) This project is an experimental, numerical, and field study of the fluid mechanics of particle removal by suspension - feeding bivalve mollusks. The effects of bivalve feeding currents on particulate transport processes in boundary-layer flows are the main focus of this study. The importance to estuarine ecology of particle removal by filter feeders stems from the hypothesis that this process can represent an important natural control on the eutrophication of estuaries that would otherwise result from nutrient inputs. Much of the work is being carried out on collaboration with USGS scientists studying the ecology of San Francisco Bay.

- A Study of the Structure of the Near-Coastal Zone Water Column using Numerical Simulations - Koseff, J. R., Ferziger, J. H., and Monismith, S. G. (ONR) The primary objective of this work is to do Large Eddy Simulations of the flow structure in the stratified water column in the near-coastal zone which are typically subject to surface heating fluxes, wind stirring, and tidally generated bottom turbulence. To do this we shall use the LES code developed by Garg et al as part of ongoing work supported by the ONR. The code which is currently being used to study the structure of a stratified channel flow is being modified to allow for surface heat fluxes, and a free-slip surface. Because of the complexity of even this idealized version of the problem we are also examining two "model" problems as well: the first is a sheared, stratified flow subject to mean strain, and the second is a stratified interface subject to two sources of turbulence. The LES code is a parallelized Navier-Stokes code for solving stratified, turbulent channel flows. This code has recently been ported to the 400 node Intel Paragon XP/S supercomputer at SDSC. The sheared, stratified flow problem is being done using a modified form (to include effects of buoyancy) of the spectral code developed by Rogallo at NASA-Ames. In the past this code has been used to perform two- and three-dimensional simulations of the interaction of internal waves with a critical layer, simulations of single and multiple triad interactions, and sheared, stratified turbulence.

- Studying the effects of source-specific gas and particulate emissions on global climate and atmospheric composition - Jacobson, M.Z. (NASA) This is a project to study the effects of controlling current and future anthropogenic gas and particulate emissions on global climate and atmospheric composition. The proposal involves the development of current and future global anthropogenic gas and particulate emission inventories by source category and the global simulation of the climate response and atmospheric composition resulting from changes in emissions. The overall goal of the study is to improve our understanding of the effects of different gas and particle emission sources on climate and on atmospheric composition. The research is a collaborative effort among scientists at Stanford University and Argonne National Laboratory. For this study, up-to-date and estimated future global emission inventories for all important gas and particle components from biomass burning, coal, natural gas, biofuel, diesel, and gasoline, will be developed. The inventories will be used, together with existing inventories from other gas and particle

sources, in an air-pollution/climate model to examine effects on global climate and atmospheric composition. Such a study is important from a scientific and policy perspective. It will try to address questions such as, what are the time-dependent combined effects of biomass-burning gases and aerosol particles on climate and what are the time-dependent climate effects of combined gas- and aerosol particle emissions from diesel vehicles, gasoline vehicles, power plants, and indoor biofuel/coal burning. This study will also enable an examination of the global distribution of gas and particle components. It will allow an examination of the climate response of nitrogen oxide (NOx) and reactive organic gas (ROG), methane, and carbon monoxide emissions through their feedback to tropospheric ozone and secondary particulate matter.

- The potential effects of hydrogen fuel cell use on climate, stratospheric ozone, and air pollution - Jacobson, M.Z. and Golden, D. (GCEP) This is project to study the potential effects on global and regional climate, stratospheric ozone, and air pollution of replacing fossil-fuel based vehicles and electric power plants with those powered by hydrogen fuel cells, where the hydrogen is produced either from steam reforming of methane, coal gasification, or wind energy. This study is important because conversion to hydrogen is certain to have impacts (positive and negative) on the atmosphere, yet no study has examined such potential impacts with a numerical model that has replaced current and future fossil fuels emissions with hydrogen-related emissions in an actual emission inventory nor with a numerical model that treats gases, aerosols, meteorology, and radiation simultaneously over a three-dimensional global grid that nests down to the urban scale. The model to be used will be driven by emissions. For the U.S., the U.S. National Emission Inventory, which considers 370,000 stack and fugitive sources, 250,000 area sources, and 1700 categories of onroad and nonroad vehicular sources (including motorcycles, passenger vehicles, trucks, recreational vehicles, construction vehicles, farm vehicles, industrial vehicles, etc.), will be used. For the rest of the world, a set of existing inventories, each with future emission factors applied, will be used. In both cases, the inventories will be updated for future years with Intergovernmental Panel on Climate Change future emission factors. For the study, emissions from vehicles and electric power plant emissions in the inventories will be replaced with those resulting from hydrogen generation and hydrogen fuel cell use. Emissions from the use of hydrogen will include leaked hydrogen, water vapor, products of energy used to compress and/or liquefy hydrogen, products of steam reforming of methane (and of all steps in methane production), products of coal gasification (and of all steps in coal production), and products of wind energy generation (e.g., from turbine manufacturing). Base case model predictions will be evaluated against an array of gas, aerosol, and meteorological measurements. Sensitivity studies, in which vehicles and electric power plants are switched to hydrogen, will be analyzed in terms of their resulting effects on climate, stratospheric ozone, and air pollution. The outcome of this study will be a comprehensive assessment of the potential effects of converting vehicle and electric power sources in the U.S. and worldwide to hydrogen on the atmosphere.

- Using satellite data and models to study the effect of global climate on regional pollution and vice versa - Jacobson, M.Z. (NASA) This is a project to use satellite data with models to examine the effects of regional pollution on the global atmosphere and the effects of global chemical and climate change on regional air quality. The project involves three major task areas: gathering and gridding appropriate satellite and in-situ data for comparison with models, comparing models on the global and regional scales with the satellite retrievals and the in-situ data, and using the models to address the main issue listed. The effect of global chemical and climate change on regional air quality will be evaluated with a nested global-through-urban scale air pollution/climate/weather forecast model. Baseline simulations for 2001 will be run and compared with satellite retrievals, sounding data, and with data from a network of several thousand near-surface monitoring stations. The global portion of the model will then be applied to simulate changes in climate over multiple years due to estimated changes in greenhouse gas and particulate emissions determined from Special Report on Emission Scenarios (SRES) scenarios. The effects of climate change on air pollution in the nested grids will be evaluated in years 20 and 50. Simulations will be affected by estimated changes in future global emissions. The effects of regional pollution on the global atmosphere will be examined by first comparing results from two regional models with satellite data and in-situ measurements from a field campaign, then examining the fate of the pollutants as they exit from the urban/regional to larger scale. Sensitivity tests will be run under both current and future climate and emission conditions to examine the relative importance of different organic gases, emitted on the urban/regional scale, on export of ozone and aerosols to the large scale. Sensitivity tests will also examine the effect of model grid resolution and subgrid treatment on ozone and aerosols venting and dilution from the urban to larger scales.

- The dynamics of turbulence and vorticity under breaking waves - Monismith, S.G. (NSF) This laboratory experiment is aimed at understanding the nature and mechanisms of turbulence production by breaking surface waves, as they might be found in the open ocean or in lakes or estuaries. In the lab, breaking waves are produced by focusing a chirped packet of waves producing a repeatable breaking event at the focal point. Flowfields in this region are recorded with a digital video camera and are processed using an in-house particle tracking technique to calculate velocity fields. Many repeats of the breaking event are used to build up ensemble averages of the resulting turbulent flow, from which inferences about the dynamics of this complex, unsteady flow can be made.

- A Study of the Structure of Stratified Tidal Flows - Monismith, S.G. (NSF) This project consists of field studies of turbulent stratified flows in San Francisco Bay. These studies are carried out in collaboration with the USGS California District Office of the USGS. Field work involves long and short term deployment of ADCPs and CTDs to record the temporal and spatial variability of the salinity and velocity fields at specially chosen sites in northern SF Bay. These fixed deployments are supplemented by 30 hour intensive studies in which various ADCP/CTD transects are taken to better define flow structure. During these short term studies, a 5 Beam

ADCP is also used to record turbulence quantities, including the fluctuating vertical velocity. The principal question driving this work is the extent to the flow dynamics are locally one-dimensional, i.e. to the role played by lateral variability in flow properties between shoals and channels.

- Modeling and Field Studies of Chemical Plumes in Benthic Boundary Layers - Monismith, S.G. and J.R. Koseff (ONR) A joint effort withTom Powell from U.C. Berkeley, this project combines field and modeling studies to assess the rate at which chemical plumes from near-bed sources are diffused in common coastal environments and how that rate depends on hydrodynamic parameters like flow speed or wave characteristics. The field work is being done as a part of the Chemical Sensing in the Marine Environment (CSME) program at San Clemente Island, off the California coast near San Diego. Modeling is aimed at assessing our ability to predict the structure of the concentration field downstream of a well-defined source so that those factors that most influence chemical delectability in coastal environments can be determined.

- Circulation Modeling of the Sacramento-San Joaquin Delta - Monismith, S.G. (unsponsored) This project aims to apply the two-dimensional circulation model, TRIM2D developed by Vincenzo Casulli of the University of Trento and Ralph Cheng of the USGS, to modeling flows in the delta of the Sacramento-San Joaquin rivers and the adjoining part of San Francisco Bay. The principal focus of this work is on understanding the dynamics of low-frequency coupling between the Bay and Delta, and to assess the role of ÒtopologicalÓ dispersion, i.e., dispersion due to tidal flows through the complex network of channels that make up the Delta, to the overall salt balance and to the transport of organisms in this part of the San Francisco Bay estuary.

- Hydrodynamic Interactions between Olfactory Appendages and Odor Plumes - Koseff, J.R. (ONR). Many marine organisms that use water-borne chemical signals to locate prey or conspecifics have olfactory appendages bearing arrays of chemosensory receptors. Some olfactory appendages are simple rods while others have sensory hairs in various arrangements. The interaction of an appendage with ambient odor plumes and the small-scale velocity field near the appendage's surface determines the rates and locations at which molecules are encountered. Our objectives, therefore, are to determine how the flow micro-environment around these appendages, and the odor-encounter potential of appendages, is affected by i) the presence and arrangement of sensory hairs, and ii) the flicking of the appendages. We will compare the flow microenvironment and molecule capture by olfactory appendages bearing sparse, dense, or no hairs (crustacean antennules; opisthobranch rhinophores). This involves using realistic, dynamically-scaled, physical models to study effects of appendage morphology and kinematics on flow fields near sensor surfaces, and novel flume experiments with odorants leaching from benthic "prey" exposed to waves to measure, and compare, molecule encounter by flicking vs. stationary appendages. State-of-the-art hydrodynamic measurement techniques will be used to characterise the flowfield and turbulent mass transport around the appendages.

- Characterization and Modeling of Plumes and Animal Plume-Tracing in Wave-Influenced Coastal Environments - Koseff, J.R. and S. G. Monismith (ONR). We are studying the search algorithms used by benthic marine animals when finding an odorant source in wave-influenced coastal flow domains (where instantaneous velocities change direction on a time scale of seconds) versus those used when plume-tracing in unidirectional flow. By quantifying the instantaneous plume environment around the olfactory antennules of the animals while simultaneously measuring the behaviors that they execute, we hope to elucidate search rules that can be implemented effectively in artificial systems designed to operate in coastal environments. Shallow coastal sites are often characterized by waves, hence both animals and automated plume-tracing devices that use water-borne chemical cues to locate objects in such habitats must find odorant sources in oscillatory flow. Plume-tracing behavioral studies to date have been done in unidirectional currents and may not yield useful search algorithms for waves. By simultaneously measuring the instantaneous plume environment and the animal's behavioral response, we propose to determine which spatial and temporal properties of chemical plumes are important to plume-tracking animals in unidirectional currents versus in the wave-dominated flow so important in coastal areas.

- Boundary Layer Mixing and Circulation Over Rough Topography: Flow Over Coral Reefs. – Monismith, S.G., A. Genin (Hebrew University), J.R. Koseff, M.A. Reidenbach (Bi-National Science Foundation) This research entails field studies conducted in Eilat, Israel, the Red Sea to study the role that bottom roughness plays on mixing and turbulence in the overlying water column. The motivation for this work is the fundamental role that turbulence plays in coral reef ecology. Fluid flow acts to transport nutrients, larvae, wastes and numerous other constituents to and from a reef. The structure of the flow near the reef, within the turbulent bottom boundary layer, is related to the complex structure of the topography of a reef. This turbulent flow controls exchanges of both mass and momentum between the corals and the overlying water. In this study, flow measurements are made using Acoustic Doppler Current Profilers (ADCP), Acoustic Doppler Velocimeters (ADV), and Conductivity, Temperature, Depth (CTD) probes. Biological sampling is simultaneously conducted by deploying four sets of ten pump arrays to sample phytoplankton, zooplankton, and nutrients (nitrogen, phosphorus, etc.) throughout the water column. Detailed measurements of near-bottom turbulence give a measure of Reynolds stresses and bottom shear stresses. Mixing coefficients are measured using calculations of turbulence dissipation and shear. Combining these measurements with velocity profiles throughout the water column along with biological measurements give us a complete picture of circulation of both water and food sources in and above the reef. This data is then used to study the relation between bed roughness, mixing, and nutrient transport throughout the reef system.

- A Laboratory Study of Fine-Scale Mixing and Mass Transport Above a Coral Reef – Koseff, J.R., M. Koehl (U.C. Berkeley), M.A. Reidenbach (NSF)
  Dissolved chemical cues have been shown in the laboratory to induce settlement by the larvae of various benthic invertebrates. One such species is the nudibranch, Phestilla siboga, whose larvae metamorphose in response to a species specific metabolite from its prey, the coral Porites compressa. To determine how such chemical cues affect larval settlement in nature, a detailed understanding of how dissolved cues disperse in ambient water flow is needed. In this study, a constructed reef made of P. compressa skeletons is placed in a water flume capable of producing both a mean current and surface waves. The flow environment in the flume is driven to mimic the turbulent flow measured in the reef dominated by P. compressa in Kaneohe Bay, Hawaii. Using laser-Doppler anemometry (LDA), detailed flow fields above the constructed reef are measured. The structure of the odorant field leaching off the corals is studied using a planar-laser induced fluorescence (PLIF) technique. In this technique, rhodamine dye is spread over the surfaces of the coral and leached into the water column. The dye is fluoresced with the laser, then digitally photographed, and the resulting images are interrogated to quantify the structure and mass transport of the dissolved constituent. The fine scale spatial structure of chemical filaments from the reef not only reveals the spatial and temporal patterns of concentrations encountered by larvae, but also sheds light on how rough reef topography affects mixing processes.

- Hydrodynamics and Transport in a Giant Kelp Forest – Johanna Rosman, Jeff Koseff, Stephen Monismith (NSF) Along the coast of California, and in subtidal rocky environments in other temperate coastal regions, the Giant Kelp Macrocystis pyrifera forms dense forests that are home to a diverse assemblage of organisms, living on the seabed, in the surface canopy, and in the water column. This project focuses on understanding the physical processes that contribute to the transport of important biological quantities (food, nutrients, larva, spores) within these kelp forests. Using a combination of field and laboratory experiments, we are investigating processes that contribute to horizontal exchange between the kelp forest and the surrounding environment, and processes contributing to vertical mixing and turbulence generation within the kelp forest. Field experiments based in Santa Cruz, California, indicate that mean currents, waves and internal waves are all potentially important for transport in this system, and all may be modified by the presence of a kelp forest. In the laboratory we have constructed a 1:25 scale kelp forest to study the physical mechanisms by which kelp forests alter the mean flow and turbulence characteristics in more detail.

- Small-scale flow variability inside branched coral colonies: computations and experimental verification. NSF. PI's: Monismith S.G., Eaton J.K., Koseff J.R. and Chang S. In this work we are computing and validating variability of mass transfer rate, stress, and velocity fiedls through a single colony. The computation is done using immersed boundary method form of Large Eddy Simulation, and experimentally validated using Magnetic Resonance Velocimetry. The representation of the coral in both the computation and the experiments uses actual coral skeletons from Eilat, Israel and Hawaii which are scanned using computed tomography, or CT. Once the code has been validated, we will be generating a range of environments varying in velocity, wave period, coral canopy, and morphologies. The work we propose is a unique application of leading edge engineering and medical technologies

to biological oceanography, that presents an excellent opportunity to demonstrate how approaches drawn from disparate fields (e.g., engineering fluid mechanics and heat transfer, medical imaging) can produce substantial advances in our understanding of biological oceanography

- Coherent structures in rivers and estuaries. [DoD] (Fong, Fringer, Monismith, and Street in collaboration with University of Washington)
  Coherent structures are generated in rivers and estuaries when the flow interacts with bathymetric and coastline features or when density stratification causes a gradient in surface properties. These coherent structures produce surface signatures that can be detected and quantified using remote sensing techniques. Since coherent structures are embedded in the main flow, knowledge of their development and evolution will contain information about the characteristics of the main flow itself, which can thus be inferred from remote measurements. The objectives of our proposed research are to test the following four hypotheses:

  1. Flow parameters can be inferred from remotely-sensed signatures of coherent structures.
  2. Numerical models can be constrained with these inferred flow parameters.
  3. The effect of stratification on the strength of coherent structures can be used to detect the presence or absence of stratification and the location of the fresh/salt water interface.
  4. Numerical and field experiments can be used together to predict, interpret, characterize and understand coherent structures.

  In order to test the hypotheses above, we will conduct field experiments consisting of both in situ and remote sensing measurements coupled with numerical modeling experiments. The measurements, as with the numerical modeling, will focus on two scales: a local scale relevant to the generation of coherent structures and an estuary scale at which the mean flow conditions at the local scale are set. Based on the results from these measurement campaigns, we will classify and extend the current knowledge of the physics of coherent structures and use this information in a predictive capacity to inform future modeling efforts.

- Studies of flow and turbulent mixing over complex terrain - Street, R., Ludwig, F. & Chow, F. [NSF] The primary objective of this research is to refine and use Large Eddy Simulation (LES) to understand small scale atmospheric flow phenomena and to make application of these simulations to valley-scale projects. The Terrain-induced Rotor Experiment [T-REX] is the main field project of interest. We are undertaking both numerical simulations and specific field measurements as part of that project. NSF has provided a grant supplement to support interaction with Prof. Chow at the University of California-Berkeley for this work. Key elements of our four year project are: (1) extension of turbulence models of the subgrid-scale motions to allow accurate simulation in the domain of Very Large Eddy Simulation (VLES). (2) development of a comprehensive land-surface module that merges soil type with vegetation data to provide better surface characterization at high resolution. (3) examination of the impact of lateral boundary conditions on limited area forecasts. (4) simulation of the flows in the rotors in Owens Valley as part of T-REX. (5) Statistical analyses to assess simulation performance and to analyze patterns of motion at different scales.

- ROMS and SUNTANS Continued Development and Support of AESOP and NLIWI - Fringer, O., Street, R., Gerritsen, M. [ONR]
  Continued code development will occur for both the ROMS and SUNTANS codes in all aspects of this project, including code development for the SUNTANS/ROMS intercommunication. Implementing higher order TVD schemes in SUNTANS for accurate scalar advection and modifications to the SUNTANS code in order to improve wind/wave/boundary forcing and data assimilation techniques are on the agenda. Between ROMS and SUNTANS we expect to make considerable advances in the comparative evaluation of our different algorithmic approaches, expecting that this will spur further refinements on both sides. Our scientific focus is on sub-mesoscale dynamics, both for balanced flows (fronts, vortices, and turbulent cascades) and for nonlinear internal wave processes. With our codes and their embedding capabilities we expect to be able to span a wider range of scales (i.e., looking at gyre, region, mesoscale, sub-mesoscale, and finescale mixing linkages), as well as bring what we expect to be better algorithmic performance to the simulated phenomena. The first two years of the coupling project will focus on a high resolution analysis of internal waves and mesoscale and sub-mesoscale currents on the West Coast in support of the AESOP goals, with special attention focused on Monterey Bay. The ultimate goal of the coupled system will be to employ it in the South China Sea in support of NLIWI.

- Simulation of Benthic Ripples and Transport Processes for SAX - Fringer, O., Street, R. [ONR] Our goal is to provide a complete simulation code that will represent and predict the sediment transport and bed features on the continental shelf at user-specified resolution by using state-of-the-art algorithms for the physics and numerics of the simulation code. Our tools are the SUNTANS [Fringer, et al., 2006, Ocean Modelling] and PCUI [Cui and Street, 2004, Environmental Fluid Mechanics] nonhydrostatic Navier-Stokes solvers and sediment transport algorithms based on the work of Zedler and Street [JHE, 2001 & 2006]. Our primary objective is to simulate the ripple climate on the bed of the inner shelf at depths on the order of 20 m and over domains ranging from centimeters to kilometers in support of the SAX experiments and analyses. Our secondary objective is to use simulation to better understand the physics of ripple formation and sediment transport in this environment.

Hydrology and Water Resources

- The Water Supply of the Bay Area during Prolonged Droughts - Kitanidis, P. K. (UPS Foundation) The economy of the Bay Area has been booming and new housing developments can be found to the edges of the Central Valley. Is there sufficient water to support the existing population and such development rates? The purpose of this research is to study the sources, availability, and reliability of water for the greater San Francisco Bay Area, with emphasis on drought conditions. An additional objective is to evaluate the need for gradual water rationing as a drought progresses. The project includes statistical analysis of time series of major sources, demand projections, the study of conservation and rationing policies, and the conjunctive use of groundwater and surface water.

- Conditioning Model Predictions on Data and Solution of Inverse Problems in Contaminant Hydrogeology - Kitanidis, P. K. It is difficult to predict pollutant concentration in geologic formations. However, by making sensible use of data, one can improve the accuracy of predictions of models of mass transport and chemical fate. In practice, the available observations are not sufficient for predicting a unique scenario, as in the deterministic approach. The probabilistic approach aims to simulate an ensemble of scenarios that are consistent with the physical laws that govern representations of the flow, transport, and transformation, as well as the available observations. These predictions are useful in risk analysis and management, such as selecting the most cost-effective remediation scheme or sampling strategy. We develop and test new methods for incorporating the information contained in observations to: (a) Estimate hydrogeologic parameters that control rates of groundwater flow and the transport and transformation of chemicals in the subsurface, (b) Generate an ensemble of equally likely chemical concentrations consistent with process understanding and observations.

- Management of Stochastic Dynamic Systems with Emphasis on Reservoir Operation – Kitanidis, P. K. (DOE/AWU) Even when existing water-resource systems are managed efficiently, it is hard for trial-and-error heuristic management to keep up with changing demands and management objectives. Mathematical modeling and optimization could contribute to improved management, but existing procedures are limited in their effectiveness and acceptance, partially because they do not account properly for hydrologic and demand uncertainty. However, recent advances in algorithms and increases in computer power have made some problems tractable without resorting to inappropriate simplifying assumptions. We have been working to develop and apply methods that allow treatment of previously unsolvable optimization problems, including the conjunctive management of groundwater and surface water systems. The algorithms we have developed for multi-dimensional stochastic dynamic programming problems are the fastest available.

- Diffusional Rate Limitations in Heterogeneous Porous Media: Model Structure, Scale, and Geologic Characterization - Freyberg, D.L. and P.V. Roberts (EPA) This recently completed project focuses on elucidating the nature and environmental significance of both physico-chemical and apparent diffusional rate limitations during solute transport in saturated, heterogeneous porous media, with a view to evaluating the role of diffusional limitations in contaminant remediation. The research considers the relative importance of diffusion and slow advection manifested over a range of spatial scales, from the grain scale up to regional scales, within the context of analytical and numerical transport models that account for advection, diffusion, dispersion, and sorption

- Strategies for Maintaining Open Water in a Rapidly Sedimenting, Small Reservoir - Cohen, P.S. and D.L. Freyberg (Packard Foundation) Searsville Lake is a small reservoir on Stanford's Jasper Ridge Biological Preserve which is rapidly filling with sediments from the Corte Madera Creek watershed. The reservoir provides important avian habitat and is used actively in both research and teaching at the Preserve. This project is exploring opportunities to manage the sediment flux tthrough Searsville Lake so that a modest amount of open water can be maintained in the reservoir.

- Assessing the Water Balance for Large Ephemeral Streams in Arid Environments - Freyberg, D.L. (USGS student support) Ephemeral channels in arid and semi-arid environments are an extremely important hydrologically and ecologically. Flow in ephemeral channels is complex, involving short, rapidly rising and falling hydrographs, significant sediment and debris transport, and nearly complete infiltration of the flow over a channel reach. Closely coordinated with an ongoing USGS field data collection project, this dissertation research couples field data with numberical modeling in an attempt to better characterize and predict groundwater recharge from ephemeral channels.

Transport and Fate of Contaminants in the Atmosphere.

- Indoor Air Pollution and Health in Developing Countries: An Intervention Study in Bangladesh" -- N.G. Miller and L.M. Hildemann (Environmental Venture Fund, Woods Institute for the Environment)
  Half the world's population relies on dung, brush and wood as their primary source of energy for cooking and heating, and biomass combustion indoors is viewed as a major contributor to indoor air pollution in developing countries. Indoor air pollution has been shown to be associated with acute respiratory infections -- in fact, the World Health Organization has attributed 5% of all female deaths in the developing world to indoor air pollution. This project aims to assess the short- and long-term effectiveness of various social and economic incentives at inducing rural villagers in Bangladesh to acquire and use an improved cookstove. The health benefits of the improved cookstove will be assessed by measuring the real-time exposure of the cook to indoor particulate matter (smoke) before and after changing cookstove technologies.

- Real-Time Monitoring Experiments to Investigate the Differences Between Personal Exposures and Indoor Air Quality – Switzer, P., and Hildemann, L. M. (Center for Indoor Air Research) Direct measurements of personal exposure to air pollutants have been found to be 2-10x as high as concentration levels measured using stationary indoor monitors. This study will systematically investigate this so-called "personal cloud" effect by collecting temporally- and spatially-resolved measurements under carefully-controlled experimental conditions in actual indoor environments. By performing statistical analyses on this data we hope to identify the major causes of these elevated personal exposures.

- Building Ventilation Design and Indoor Air Quality- Hildemann, L. M. (UPS Endowment) Individuals spend ~90% of their time indoors, where the concentrations of airborne particles like molds, fungi and pathogens can be much higher than outdoor levels. It has been hypotehsized that ventilation systems may play an important role in propagating and disseminating these "bioaerosols". This study will measure bioaerosols within and eminating from indoor ventilation systems, to investigate what factors influence the types and concentration levels of molds and fungi present.

- Characterization of Particulate Matter Generated from the Operation of Motor Vehicles- Hildemann, L. M. (Ford Research Foundation) Increasing regulations on particulate matter (PM) emissions over the next decade are expected to impact the motor vehicle industry. A major issue.is whether these new regulations will be based on the mass, the number,or the chemical composition of the PM. This research will examine and develop new technologies for measuring the chemical composition of PM in modern-day motor vehicle emissions.

- Studying the Mixing State of Aerosols and Its Impact on Global Climate - Jacobson, M. Z. (NSF) The goal of this project is to analyze the effect of the mixing state of aerosols on global and regional direct forcing and temperatures. One scientific question to be addressed is, what is the global- and regional-scale mixing state of aerosol-particles and what is the resulting direct radiative forcing? A second question is, which feedbacks of aerosol-particles to climate are important and which ones are not? A third question is, what are the climate effects of (a) fossil-fuel soot and organic matter, (b) biomass burning gases and particles, (c) sulfur dioxide and resulting sulfate, and how do the effects of these components compare with the effects of CO2 and CH4?

- Studying the Effects of Ca, Mg, and K on Aerosol Size and Composition, NOy, and Radiative Transfer - Jacobson, M. Z. (NASA). This is a project to study the effects of calcium, magnesium, and potassium on aerosol size and composition. These chemicals, present in soil dust and/or sea spray, have been found to have an important effect on aerosol size distributions in and relatively clean air, shifting nitrate from the coarse mode to the accumulation mode. For this study, the feedback between these chemicals on radiative parameters, such as UV, total solar, and infrared irradiance and top-of-the-atmosphere radiative forcing will be examined. The calculations will also be coupled with gas-phase chemistry to estimate the effects of Ca, Mg, K, and total aerosols on gas-phase NOy concentrations. The purpose of this exercise is to estimate the extent to which aerosols as a whole and individual aerosol components affect the NOy:NOx ratio, which is typically overpredicted in many models.

Transport and Fate of Contaminants in Groundwater

- Analysis of Halogenated Organic Particle-Scale Desorption via Column Studies and C-13 Solid State NMR Spectroscopy – Reinhard, M. (EPA). Research has shown that a significant fraction of organics sorbed to soils and sediments (geosorbents) resists desorption. This fraction is not amenable to conventional treatment and needs special consideration in fate and transport assessment. In this project we identify sorbent properties that govern slow desorption and compare results of desorption studies with predictions based on mechanistic models. The approach is to artificially contaminate geosorbents with TCE, deuterated TCE and/or PCE either individually or as mixtures and to quantify rate of desorption as a function of initial sorbent loading and desorption conditions. Data suggest that the sorption sites of the slow desorbing fraction reside in micropores and that diffusion of is sterically hindered.

- Field-Testing of Palladium-Catalyzed Hydrogenation for Chlorinated Hydrocarbon Removal – Reinhard, M. and Roberts, P. This project aims to evaluate palladium catalyzed hydrodehalogenation using hydrogen gas as a method for removing halogenated hydrocarbon compounds form contaminated water. Preliminary studies indicate that hydrodehalogenation proceeds under mild conditions when facilitated

by a palladium catalyst. The project goal is to gain operational experience with the H^2/Pd process under field condtions. Specifically we aim to: 1) quantify catalyst efficacy; 2) identify and minimize the factors contributing to catalyst fouling; 3) measure competing reactions and determine their hydrogen consumption; 4) evaluate the need for pretreatment; and 5) determine how best to supply hydrogen safely and economically. Results will be used to optimize the process, provide design criteria, and evaluate cost effectiveness compared with alternative treatment methods.

- Diffusional Rate Limitations in Heterogeneous Porous Media: Model Structure, Scale, and Geologic Characterization - Freyberg, D.L. and P.V. Roberts (EPA) This recently completed project focuses on elucidating the nature and environmental significance of both physico-chemical and apparent diffusional rate limitations during solute transport in saturated, heterogeneous porous media, with a view to evaluating the role of diffusional limitations in contaminant remediation. The research considers the relative importance of diffusion and slow advection manifested over a range of spatial scales, from the grain scale up to regional scales, within the context of analytical and numerical transport models that account for advection, diffusion, dispersion, and sorption.

- Strategies for Maintaining Open Water in a Rapidly Sedimenting, Small Reservoir - Cohen, P.S. and D.L. Freyberg (Packard Foundation) Searsville Lake is a small reservoir on Stanford's Jasper Ridge Biological Preserve which is rapidly filling with sediments from the Corte Madera Creek watershed. The reservoir provides important avian habitat and is used actively in both research and teaching at the Preserve. This project is exploring opportunities to manage the sediment flux tthrough Searsville Lake so that a modest amount of open water can be maintained in the reservoir.

- Assessing the Water Balance for Large Ephemeral Streams in Arid Environments - Freyberg, D.L. (USGS student support) Ephemeral channels in arid and semi-arid environments are an extremely important hydrologically and ecologically. Flow in ephemeral channels is complex, involving short, rapidly rising and falling hydrographs, significant sediment and debris transport, and nearly complete infiltration of the flow over a channel reach. Closely coordinated with an ongoing USGS field data collection project, this dissertation research couples field data with numberical modeling in an attempt to better characterize and predict groundwater recharge from ephemeral channels.

- Engineering Pedagogy--Teaching Turbulent Diffusion in Engineering Fluid Mechanics - Freyberg, D.L. and J.R. Koseff (NSF student support) This doctoral research project focuses on the pedagogy of engineering fluid mechanics, in particular, teaching and learning the concept of turbulent diffusion. Closely coupled with laboratory research studying the role of turbulent diffusion in the foraging behavior of lobsters, this doctoral project is using advances in science education, cognitive science, and psychology, along with carefully designed experimentation and testing, to develop effective teaching techniques for a key, difficult concept in fluid mechanics.

- Characterization and Modeling of Sorption Processes for the Nevada Nuclear Waste Storage Investigations – Leckie, J. O. (Los Alamos National Laboratories) The objectives of this research is to investigate the adsorbtive behavior of the uranyl and neptunyl ions in aqueous systems continuing goethite, hematite and, possibly, feldspars. These studies will include experimental work with competing ligands (e.g., carbonate, EDTA, natural humics) as well as studies to investigate competitive behavior with calcium and magnesium. The resulting data will be modeled using surface complexation models.

- Radionuclide Speciation in Heterogeneous Aqueous Geochemical Environment – Leckie, J. O. (Sandia National Laboratory) This project is concerned with experimental and theoretical studies of the interaction of radionuclides with mineral/solution interfaces likely to be found in the WIPP site high level waste repository. The experimental part involves both time dependent and equilibrium studies of neptunyl and uranyl ion interactions with clays and hydrous iron oxides over a range of ionic strengths (1 x 10-3M - 3M) and in the presence of competing ligands. The theoretical aspects are concerned with the development of modeling approaches for adsorbate interactions with clay surfaces.

- The Fate and Transport of Wastewater Indicator Compounds During Groundwater Recharge with Water of Wastewater Origin – Reinhard, M. (Orange County Water District). In many water-short areas treated effluents are often the only alternative to augment existing water supplies. Increasingly, effluents are treated so that they can be percolated into the ground to augmented depleted aquifers. This project aims to assess the microbial, chemical and physical processes that affect the fate and transport of anthropogenic contaminants during water percolation and groundwater transport. The data will be useful for developing models that predict the water quality of recharge water as a function of source water quality, soil type, residence time in the ground, and travel distance. Such models will serve to develop science-based regulations for artificial water reuse operations.

- Particle-Particle Interactions in Marine Systems: Steady-State, Continuous Flow, Aggregation Studies – Leckie, J. O. (NSF) Four linked objectives highlight this proposed study of aggregation/sedimentation dynamics. First, a new type of laboratory apparatus will be developed to allow previously unachieved simulation of a continuous flow, steady state system. The simulation apparatus is designed for study of real time aggregation from the simplest processes to relatively complex, biologically mediated processes in controlled, reproducible conditions. Second, two innovative particle size measuring technologies are proposed which allow noninterfering observation of aggregation/sedimentation dynamics. Development and adaptation of these techniques aims at avoiding the sampling artifacts, limited size range and restrictive fluid and particle requirements inherent in many traditional measuring techniques (i.e., electrozone, settling rate). Third, an experimental sequence is suggested which uses controlled variations of particle type, surface chemistry and fluid conditions to assess the interplay of physical, chemical and rudimentary biological factors that have been scantly addressed by previous research. Particular effort is devoted to elucidating both the unique and interactive mechanisms by which exopolymers from selected marine organisms enhance or retard aggregation. Fourth, laboratory findings will be modeled to provide a usable tool for future predictive, design, and analytical work.

- Pore-Scale Hydrodynamics and Physicochemical Transport. Constitutive Relations of Solute Transport and Transformation at the Darcy Scale – Kitanidis, P. K. (WRHSRC, NSF, DuPont) In terms of physico-chemical fundamentals, the transport and transformation of reactive solutes is most satisfactorily understood and quantified at the pore scale. However, this scale is too microscopic for almost all practical applications. In practice, the smallest scale for modeling the transport and chemical fate of solutes in porous media is the laboratory or Darcy scale, which is much larger than the pore scale. At the Darcy scale, a complex medium that actually consists of pores, a solid matrix with biofilm, etc., is replaced by a homogenized medium characterized by constitutive relations among macroscopic variables and parameters. The general advection-dispersion-reaction equation, which is the starting point of every practical modeling effort, is based on these relations and parameters and purports to describe the transport behavior of a concentration spatially averaged over a block of the order of at least centimeters. What is the appropriate form of this equation and what parameters should be used? This research aims at providing answers to these questions. The methodology followed is to model flow, transport, and chemical transformations at the pore scale and then to scale up in order to derive constitutive equations and parameters. The constitutive equations and parameters to be obtained will thus be consistent with the fundamental physico-chemical principles as well as the heterogeneity of the medium. The longer-term objective is to promote a firmer understanding of the factors that control the transport and chemical fate of pollutants, substrates, and electron acceptors at the Darcy scale.

- Factors Controlling Solute Dilution in Heterogeneous Formations – Kitanidis, P. K. (NSF, SGF) Although the effect of heterogeneity on the spreading of contaminant plumes has been studied, the effect of heterogeneity on dilution remains to be determined, especially at "early" times relevant in tracer tests and remediation projects. Dilution is measured by the peak concentration and the volume occupied by solute. Spreading is quantified by the spatial second moment of the concentration distribution. In assessing environmental impacts of groundwater contamination, it is important to be able to anticipate peak concentrations, not just the spatial extent of contamination. We conduct theoretical analysis, detailed numerical simulations, and comparisons with field data. Contaminant dilution measures are related to the porous media constitutive parameters and, primarily, the variability of hydraulic conductivity and the local dispersion. Predictions of dilution are made via analytical approximations, which lead to predictive partial differential equations. The approximations validity is assessed through numerical simulations and the results are evaluated by comparison with results from field experiments. Objectives: (a) a better understanding of the time-evolution of contaminant concentration levels, and (b) guidelines to the practitioner for assessing dilution of contaminants in heterogeneous geologic formations.

- In Situ Stabilization of Persistent Organic Contaminants in Marine Sediments - Luthy, R.G., U. Ghosh, R.N. Zare and collaborators at the US Army Engineer Research and Development Center, Vicksburg, MS and the University of Notre Dame (US Department of Defense, Strategic Environmental Research and Development Program) The addition of coal-derived sorbents is being evaluated as a treatment technology to reduce the bioavailability and toxicity of polychlorinated biphenyls [PCBs] and polycyclic aromatic hydrocarbons [PAHs] in sediments. This work

comprises a suite of tests with contaminated sediment from Hunters Point Naval Shipyard, San Francisco Bay.

- Contaminated Sediment Processes and Bioavailability - Luthy, R.G., S.G. Monismith, D. Epel and R.N. Zare (Stanford University Bio-X Interdisciplinary Initiative Program and collaborators at the US Geologic Survey, Menlo Park, CA) Organic contaminants in sediments pose long-term risks to human health and the environment. This project seeks to understand how the binding of organic contaminants with sediment particles affects the uptake and accumulation of polychlorinated biphenyls [PCBs] and polycyclic aromatic hydrocarbons [PAHs] by particle-feeding organisms, such as clams native to San Francisco Bay.

- Characterization of Lampblack Materials in Soils - Luthy, R.G. (Gas Technology Institute, Chicago, IL) Lampblack was produced as a by-product from the former oil gasification processes used in California. The distribution and binding of polycyclic aromatic hydrocarbons [PAHs] in lampblack material from field sites are studied to assess how this material binds the PAHs and reduces exposure.

- Microscale Characterization of the Binding and Sequestration of Nitroaromatics in Soils - Luthy, R.G. and U. Ghosh (US Army Engineer Research and Development Center, Vicksburg, MS, and University of Notre Dame) Microscale analytic techniques are applied to soils contaminated with TNT to assess whether crystalline TNT exists in the soil and how this affects the biotreatability of TNT-impacted soils from Army ammunition sites.

- PAH and PCB Binding to Sorbent Material - Luthy, R. G. (Ford Motor Company) Mass transfer and phase partitioning studies are evaluating the rate of transfer of PAHs and PCBs from contaminated sediment to sorbent material.

- Cyanide Measurement and Chemistry in Wastewater Effluent - Luthy, R. G. (Water Environment Research Foundation and others; with Carnegie Mellon University, Malcolm Pirnie, Inc and Clarkson University) A multi-investigator project is evaluating cyanide measurement and speciation at low levels in chlorinated effluent. The effect of chlorination on possible formation of cyanide at low levels is studied. The collaborators include various large municipal wastewater treatment plants across the United States. (with David A. Dzombak, Carnegie Mellon University)

- Mobility of PCBs in Contaminated Soils/Sediments - Luthy, R. G. (US EPA) A novel passive, wick sampler is designed to measure hydrophobic organic compounds in soil pore water. Laboratory tests assess the device's hydraulic performance and capture efficiency for chlorinated aromatics. The role of separate phase oil containing PCBs is modeled to evaluate the release of PCBs from hydraulic oils in sediment and soil (Sean McNamara).

Contaminant Control Technology

- Toxic Trace Metal Removal Processes – Leckie, J. O. (WRHSRC, EPA) General project objectives are to study the adsorption/desorption characteristics of toxic metals and metalloids, including radionuclides as well as stable isotopes, under conditions where competing organic ligands are present and where remobilization might occur (e.g., contaminated ground water systems, mixed industrial wastes). The investigation will focus on several of the following: Cd, Ni, Pb, Cr, Cu, Co, As, and/or Se. The selection of organic ligands will include commercially used sequestering agents (e.g., EDTA) as well as metabolic products from microbial degradation of organic matter. Major experimental variables are pH, temperature, type and concentration of solid, organic ligand and ionic strength. In addition, the fundamental aspects of adsorption reactions of trace metal ions within the pores of porous particles will be studied. This aspect of the study will focus on cases where overall rate of adsorption is limited by internal mass transport constraints. Part of the intent in studying the internal mass transport limited adsorption is to define the chemical and physical limitations of the adsorption process as a function of pore size distribution and to describe the observed phenomena in a mathematical format.

- In Situ Anaerobic Bioremediation of Fuel Contaminated Ground Water – Reinhard, M. (Office of Naval Research). Ground water contaminated with fuel is typically anaerobic. Under these conditions, microorganisms will use alternate electron acceptors in the order nitrate, sulfate, and carbon dioxide to degrade petroleum derived contaminants. This project aims to demonstrate and evaluate the efficacy of *in situ* bioremediation that relies on the addition of low doses of alternate electron acceptors. The approach is to amend a contaminated zone of an anaerobic gasoline plume with mixtures of alternate electron acceptors and to observe the enhanced removal of hydrocarbon contaminants. The data will be used to demonstrate the technical viability of anaerobic bioremediation approaches.

- Palladium Catalyzed Reduction of Water Contaminants Under Environmental Conditions – Reinhard, M. (EPA). Many halogenated hydrocarbon compounds are rapidly dehalogenated by hydrogen gas in the presence of a heterogeneous metal catalyst. In addition, catalyzed hydrogenation rapidly reduces some inorganic oxyanions such as nitrate to less toxic forms. The objective of this project to establish the mechanistic basis for designing metal catalyzed detoxification processes. The reactions that occur during simulated treatment at the catalyst surface are investigated using kinetic and surface analytical methods.

- Reductive Transformation of Chlorinated Ethenes Catalyzed by Vitamin B_{12} – Reinhard, M. (WRHSRC). Transition-metal coenzymes such as vitamin B_{12} have been implicated as the responsible agents in the respiratory of cometabolic dehalogenation of chlorinated hydrocarbon compounds. Potential biological dehalogenation pathways have been derived from studies in abiotic systems in which catalytic amounts of Ti(III) were used as the bulk reductant. The overall objective of the project is to improve our understanding of the chemistry of B_{12} mediated dehalogenation reactions. The kinetics of trichloroethylene (TCE) dehalogenation is being studied in abiotic model systems with Ti(III) as the reductant and B_{12} as the catalyst. The results obtained in abiotic systems are compared with results obtained in biological systems.

- Heavy Metals Incorporation into Ceramic Crystalline Matrix – Leckie, J. O. (EPA) The objective of this project is the illucidation of the physical-chemical processes by which selected heavy metals (Pb, Cr, Cu, Co, Cd) are incorporated into the ceramic matrix during firing of clay/metal bearing sludge mixtures. Details of the bonding and location of metals in the ceramic crystalline matrix will be studied using XRD, EXAFS, XPS and SEM. Additional spectroscopic tools include NMR and FTIR. The major experimental variables are type of metal, metal /clay ratio, time and temperature of firing process.

- In Situ Treatment of Chlorinated Solvents – McCarty, P. L. (DuPont Chemicals, WRHSRC, EPA) Several species of bacteria have been isolated and identified by others that have the ability to reductively dehalogenate chlorinated aliphatic hydrocarbons (CAHs). However, an individual or group of organisms responsible for the complete dehalogenation process from tetrachloroethylene (PCE) to ethene has not yet been identified. The objectives of this study are to describe the bacterium or groups of bacteria that are responsible for conversion of tetrachloroethene (PCE) to ethene in aquifer samples taken from a contaminated site in Victoria, Texas, and to examine the factors affecting the rate and extent of transformation.

- Mechanisms, Chemistry, and Kinetics of Anaerobic Biodegradation of cDCE and VC McCarty, P.L. and Spormann, A.M. (U.S. DOE and DuPont Chemicals) Biological reductive dehalogenation of the chlorinated ethenes, tetrachloroethene (PCE) and trichloroethene (TCE) to cis-1,2-dichloroethene (cDCE), vinyl chloride (VC) and then ethene is of great interest both for natural attenuation and engineered remediation of these hazardous contaminants in groundwater. This study was directed towards a better understanding of the factors affecting the rate and extent of conversions of cDCE and VC to ethene, which are generally considered the rate limiting steps in the overall process. The objectives of this study are to (1) determine the biochemical pathways for reductive dehalogenation of cDCE and VC, including identification of the enzymes involved, (2) determine the chemical requirements, especially the type and quantity of electron donors needed by the microorganisms for reductive dehalogenation, and (3) evaluate the kinetics of the process with respect to the concentration of both the electron donors and the electron acceptors (cDCE and VC).

- Hydrodynamic and Biological Factors Affecting Aquifer Clogging During In-Situ Bioremediation – McCarty, P. L. (WRHSRC, EPA) With in-situ bioremediation processes, bacteria are stimulated to grow on substrates introduced into groundwater. When this is done, there is a potential for clogging of the aquifer by excessive bacterial growth, thus restricting the movement of groundwater and making it difficult to introduced additional chemicals. The object of this study is to learn better how clogging of aquifers occurs, and what characteristics of the aquifer, the chemicals introduced, and microorganisms contribute most to the clogging problem. In order to study these factors, a laboratory investigation is being conducted in which enhanced imaging is used to better evaluate the hydrodynamic and biological factors involved.

- Field Demonstration of Vertical and Horizontal Recirculation Wells for In Situ Treatment of Chlorinated Solvent Contaminated Groundwater – Goltz, M.N., McCarty, P.L., Gorelick, S.M., and Hopkins, G. (Strategic Environmental Research and Development Program) The purpose of this study is to evaluate the potential for removal of chlorinated organic solvents at their source in an aquifer by combining two processes, in-well vapor stripping and in situ aerobic cometabolic biodegradation. The combined system is termed

BioEnHanced In Well Vapor Stripping (BEHIVS). The system will be evaluated at full scale in the field at a trichloroethylene (TCE) contaminant groundwater site at Edwards Air Force Base.

- Development of Effective Aerobic Cometabolic Systems for the In-situ Transformation of Problematic Chlorinated Solvent Mixtures – Semprini, L., Arp, D., McCarty, P.L., and Hopkins, G. (Strategic Environmental Research and Development Program) The goal of the proposed research is to demonstrate the potential of using propane and butane-utilizing microorganisms to transform problematic chlorinated solvent (CAH) mixtures in groundwater. The demonstration at the Moffett Federal Airfield Test Site will be aimed towards recirculation well treatment systems that can be used to create bioreactive passive barriers in contaminated aquifers. Our research with microorganisms stimulated on propane or butane has demonstrated the potential for transforming a broad range of CAH mixtures that have been problematic with other cometabolic substrates. Microcosm studies conducted with subsurface solids and groundwater from contaminated DOD sites, however, have shown that propane and butane-utilizers are often absent in the subsurface, or have long lag periods before effective stimulation is acheived. The proposed work will demonstrate effective methods to create passive treatment barriers through both bioaugmentation and the use of recirculation well technology. Microbial growth and maintenance for effective cometabolic treatment will be achieved through propane or butane addition to the subsurface. In addition, we will explore the use of mixed cometabolic substrates for the treatment of problematic CAH mixtures.

Environmental Planning and Management

- How Rent Seeking, Learning and Path Dependence Shape Environmental Institutions: The Case of the Cauca Valley Corporation in Colombia – Ortolano, L. (Morrison Institute for Population and Resources Studies and the UPS Foundation)
  The Corporacion Autonoma Regional del Valle del Cauca (CVC), which was founded in 1954, is one of the most well established environmental regulatory agencies in Colombia. This study demonstrates how "rent seeking" by regional elites and others caused the CVC to move beyond its original purpose, which was to develop water resources projects, and create regulatory programs dealing with water pollution control and environmental impact assessment. The research also shows that four different forms of organizational learning affected CVC's performance as a regulatory body. The concept of path dependence is used to explain why the CVC served as a model for other regional corporations in Colombia, and why these corporations have dominant roles in implementing Colombia's environmental policies.

- Effectiveness of Subsidies for Water and Wastewater Infrastructure: Projects along the United States–Mexico Border– Ortolano, L. (National Science Foundation and the UPS Foundation) This study investigates the effectiveness of international water and wastewater projects along the Mexico-United States border. Projects under consideration are those supported by the Border Environment Cooperation Commission, North American Development Bank, and the Texas Water Development Board. In addition to considering the technical merits of these border projects, the research investigates the way the projects are influenced by local government, politics, economics, and culture. This investigation into effectiveness of wastewater projects attempts to identify best practices for addressing the root causes of inadequate environmental infrastructure along the U.S.-Mexico border.

- Japan's Role in International Environmental Protection: Clean Coal Technology Transfer to China – Ortolano, L. (National Science Foundation and the UPS Foundation) Japan is playing an increasingly significant role in environmental protection and energy development throughout Asia. This research focuses on programs to transfer clean coal technologies from Japan to China, because these programs are well established and because China depends heavily on coal as an energy source. The research focuses on the following questions related to the clean coal technology transfer programs:

  – How are these technology transfer programs being implemented, and what are the key factors influencing program effectiveness?
  – To what extent are these programs affecting energy development and related environmental protection decisions in China and Japan?
  – What is the nature of Japan's role in international environmental protection?

  This research includes case studies of demonstration projects that are part of a clean coal technology program developed by Japan's New Energy and Industrial Technology Development Organization.

- Pollution Control at Township and Village Enterprises in China – Ortolano, L. (Fulbright Commission and the World Bank) Aspects of the post-1978 economic reform in China have motivated the growth of small- to medium-sized companies. These firms are widely scattered throughout the semi-rural areas in the outskirts of many large cities in eastern China. Because there are so many small-scale enterprises and they are so widely dispersed, local environmental regulatory agencies have had problems in regulating them. This research examines the record of compliance with water pollution control requirements of small-scale enterprises in the semi-rural areas around Shanghai. It also identifies factors that contribute to and impede compliance.

- Cleaner Production at the City Level in China – Ortolano, L. The 1990's saw a shift in China's national strategy for pollution control: a change from traditional end-of-pipe treatment to cleaner production. In this context, cleaner production refers to the application of strategies to reduce the sources of pollution, and it includes measures such as technological process changes and modifications in materials and put some product specifications. On-site materials reclamation and reuse are also integral parts of cleaner production.

  Many countries have tried to promote cleaner production at the level of individual industrial sectors, but China is unique in attempting to supplemented sector level programs with programs to foster cleaner production at the level of an entire city. Indeed the State Economic and Technology Commission has required 10 cities to develop city level cleaner production programs. This research uses one of those 10 cities, Taiyuan, for case study purposes. For comparative purposes, the research also uses two cities in Jiangsu, a province in which major cities are required to implement a program of cleaner production audits. The three case studies cities are being used to investigate the contents and effectiveness of city level cleaner production programs. many foreign, bilateral, and multilateral programs involving substantial investments of resources have been established to encourage Cleaner Production in China. Evaluations of these city level cleaner production programs can help improve the efficiency and effectiveness of these investments.

- Non-Governmental Organizations in China's Wildlife Conservation Effort – Ortolano, L. (Asia-Pacific Scholar's Program) During the 1990's, environmental non-governmental organizations (NGO's) began to play an important role in the management of natural resources in China. These organizations have different characteristics (e.g., financial resources, leadership, relations with the media) and they have different political opportunities to influence environmental and natural resources management. This research explores relationships between two sets of variables - organizational characteristics and political opportunities to participate – and activities of Chinese NGO's engaged in wildlife conservation efforts. The empirical work for the study includes a survey of wildlife conservation NGO's registered with the national government and with the Beijing municipal government. The research also includes a study of NGO efforts to save the Tibetan Antelope in Qinghai Province.

- Implementing the Montreal Protocol in China – Ortolano, L. (Institute for International Studies, the World Bank and the MacArthur Foundation) Although numerous international environmental treaties have been negotiated in recent years, little systematic study has been done of whether and how signatory nations comply with those treaties. This research analyzes the ways in which China has responded to requirements it agreed to when it signed the Montreal Protocol on Substances that Deplete the Ozone Layer. The Montreal Protocol is particularly significant because it includes specific numerical targets for emission reductions and a time frame for achieving those targets. Overall compliance with the Montreal Protocol depends heavily on compliance by developing countries, especially China.

  This research details actions taken by China to implement the Montreal Protocol, and it analyzes how factors (such as financial and technological constraints, economic growth, and management capability) have influenced China's ability to meet its obligations under the Protocol.

- Reduction in Greenhouse Gases in Japanese Cities – Ortolano, L. (U.S. Environmental Protection Agency and Stanford University) Global climate change is widely recognized as an international problem. Most scientists believe that key sources of this problem are emissions of the so-called greenhouse gases, such as carbon dioxide and methane.

  Recently, the Japanese government passed a law that requires cities in Japan to develop and implement plans to control greenhouse gases. Elements of these plans include actions that municipal governments can take to reduce it quite greenhouse gas emissions, as well as changes in infrastructure, particularly transportation systems, that can achieve the same lands. This law is both unique and extraordinarily significant, since cities have the potential to play leading roles in reducing greenhouse gases. This research, which is in its formative stages, will use both case studies and survey research methods to characterize both the content and effectiveness of actions taken by Japanese cities to implement the new law .

Microbiology and Biotechnology

- Biochemistry and Genetics of Anaerobic Oxidation of Aromatic Hydrocarbons - Alfred Spormann (NSF) Oxidation of aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, and xylenes (BTEX) by anaerobic bacteria is of considerable biochemical and environmental interest. The enzymes involved in the initial degradation reactions of these substrates are dramatically different from the well-characterized aerobic oxidation

reactions: In all aerobic pathways, the initial reactions involve mono- or dioxygenases that require molecular oxygen as a substrate. Anaerobic bacteria face the biochemical problem of how to perform the first oxidation step in the absence of molecular oxygen.

From an environmental point of view, degradation of these aromatic hydrocarbons is important, because they represent major components of the water soluble fraction of gasoline fuel. Leaking underground fuel storage tanks or surface spills often release these compounds into aquifers. Through research in the recent years, two fundamentally different modes to initiate anaerobic mineralization of alkylbenzenes are emerging: Methyl benzenes are activated by addition of the methyl groyup to fumarate, and benzylsuccinate synthase represents the prototype of this reaction. Alkylbenzenes with side chain lengths of * 2 carbons are anaerobically oxidized at the methylene carbon for which ethylbenzene dehydrogenase serves as the prototype.

One focus of our research is the novel enzyme benzylsuccinate synthase which catalyzes as the initial reaction in anaerobic activation of toluene the addition of the toluene methyl group to fumarate to form benzylsuccinate: http://www-ce.Stanford.EDU:80/~spormann/Bss%20reaction.JPG

This is a unique non-redox reaction to activate methyl benzenes and also a novel mode to form a new carbon-carbon bond. This enzyme is of considerable interest because it carries an organic free glycyl radical. Biochemical and molecular studies are directed to elucidate the reaction mechanism. A similar reaction is involved in anaerobic activation of m-xylene.

The other focus is on anaerobic ethylbenzene dehydrogenase which catalyzes the first reaction in anaerobic ethylbenzene mineralization. Ethlbenzene dehydrogenase is an unusual enzyme because it catalyzes the oxidation of a hydrocarbon in the absence of molecular oxygen and converts ethylbenzene to 1-phenylethanol with p-benzoquinone as electron acceptor. http://www-ce.Stanford.EDU:80/~spormann/EBreactions.JPG

Biochemical studies are conducted with purified enzymes, and gas chromatography (GC), gas chromatography/ mass spectrometry (GC/MS), HPLC, and spectrophotometry assist in analyzing these unusual reactions.

A parallel genetic approach is directed to identify the structural genes involved and to understand the molecular mechanisms of their control. The current focus of the genetic approach is to generate mutants defective in aromatic hydrocarbon metabolism, and to isolate and to clone the genes involved by genetic complementation.

- Anaerobic trnasformation of chloroethenes and evolution of pathways for transformation of "unnatural" compounds. - Alfred Spormann (SERDP) Next to the BTEX compounds, chlorinated alkenes, such as tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE), and vinyl chloride (VC) are another important class of groundwater contaminants in the U.S.. These chlorinated aliphatic compounds are exclusively of anthropogenic origin and have been introduced involuntarily into the environment only within the last decades. Chlorinated aliphatic solvents are frequently used for the degreasing of engines and in dry-cleaning processes. PCE and TCE, but more importantly VC, are highly toxic compounds, and their concentrations in drinking water are regulated. Interestingly, under anaerobic conditions PCE and TCE are metabolized to VC, and, thus, are converted into a product that is more toxic than the parent compound. From a fundamental point of view, the microbial transformation of these compounds is very interesting because these unnatural chemicals were introduced into the environment only a few decades ago. Nevertheless, pathways that metabolize these compounds have evolved in some organisms. Thus, research on these novel microbes that can completely degrade these unnatural compounds allows us to address the more fundamental question of how

novel pathways for the degradation of unnatural compounds evolve in nature.

Recently, we discovered a novel mode of anaerobic reductive vinyl chloride transformation to ethylene. Previously known reductive dehalogenation of PCE, TCE, or chlorobenzoates were shown to involve corrinoids as the catalytically active reagent. Through inhibitor studies with cell-free extracts from an anaerobic, VC-dehalogenating mixed culture, we discovered that VC reduction to ethene does not involve a corrinoid. Current, work investigates the microbial and molecular mechanism of this novel enzymatic activity. Understanding the fundamentals of natural dehalogenation of unnatural compounds will provide crucial knowledge that will allow also the development of novel in situ strategies to specifically target biodegradation of VC to this microbial mechanism. Furthermore, understanding this mechanism may also provide tools for engineering a chemical remediation scheme, as has been done using vitamin B12-based chemical reductive dehalogenation of PCE and TCE that was first discovered as a prokaryotic transformation reaction.

In addition, a novel research approach explores the in vitro engineering of enzymes with novel catalytic properties for the transformation of recalcitrant chemicals by use of directed evolution.

- Functional Genomics and Physiology of Microbes in Biofilms - Alfred Spormann, Gordon E. Brown, Jr. (NSF) Microbial biofilms are structures where microbes are attached to a surface and embedded in an extracellular polysaccharide (EPS) matrix. Microbial biofilms form on virtually all aqueous environmental interfaces, including the surfaces of ships, pipes, and sewers, and on soil mineral particles. Biofilms are of enormous economic, medical, and biogeochemical importance. Our work is at the interface of molecular microbiology, molecular microbial ecology, and biogeochemistry.

  Biofilms are dynamic structures and undergo a developmental process consisting of (i) initial attachment, (ii) microcolony formation, (iii) maturation, and (iv) detachment. Because cells are constrained in a biofilm and because free diffusion of small molecules is affected within a biofilm, these biofilms exhibit a high degree of internal heterogeneity, where the overall biological activity of a biofilm is controlled by an intricate structure-function relationship. Therefore, individual cells, as well as the overall microbial community, respond to changes in the environment. Thus, the activity of a microbe within a biofilm is a function of its position in the biofilm.

  We are studying the cell-cell and cell-substratum intractions using a new genomic approach in conjunction with confocal laser scanning microscopy (CLSM). Our goal is to understand and to predict the complex metabolic and signaling interactions that occur between biofilm microbes. We use two model microbes, Shewanella oneidensis MR-1 and Vibrio cholerae. The genome of both microorganisms has been sequenced, and we are using DNA microarrays to generate profiles of whole cell gene expression during cell-cell and cell-surface interactions. CLSM is a powerful technology to visualize individual microbial cells in biofilms and to visualize the expression of individual genes in biofilm cells. This allows us to observe directly metabolic and signaling cell-cell interactions in active biofilms. This CLSM work is conducted here at the new Stanford Biofilm Research Center.

  S. oneidensisutilizes the surface of insoluble Fe(III) minerals as electron acceptor and forms biofilms on such minerals. The reduced Fe(II) minerals, in turn, are critically important for geochemical redox reactions involved in abiotic heavy metal mobilization and reductive degradation reactions. We are specifically

interested in the molecular processes that control S. oneidensis biofilm formation and stability, and that are involved in redox reactions between biofilm cells and the mineral subtratum.

V. cholerae forms biofilms on inorganic and organic, including chitin, surfaces. It is believed that chitin provides a critical metabolizable substrate for this microbe to persistent in marine environments. Also here, we are using a genomic approach to uncover cell-cell and cell-substratum interactions of V. cholerae in marine environments and on chitin surfaces.

This project is part of an interdisciplinary NSF-funded research effort (CREAMS) on "Chemical and Microbial Interactions on Environmental Surfaces"

- Reductive processes for the bioremediation of chlorinated solvent metal mixtures - Craig Criddle, Alfred Spormann (NIEHS). Mixtures of chlorinated solvenets and metals pose a significant challenge for bioremediation. This work focuses on the transfer of the the carbon tetrachloride degradation genes encoding production of pyridine-2,6-bis(thiocarboxylate) (PDTC) from Pseudomonas stutzeri strain KC to Shewanella oneidensis MR1 to create an organism with increased metal tolerance and the ability to dechlorinate carbon tetrachloride.

- Field-scale evaluation of biostimulation for remediation of uranium-contaminated groundwater - Craig Criddle, Peter Kitanidis, and Gary Hopkins (U.S. DOE). Microbial reduction of uranium may prevent its migration to receptor streams. However, application of this technology to field sites is untested, and future site remediation will require improved understanding of basic processes and implementation strategies in heterogeneous environments. The goals of this work are (1) to develop a predictive capability for the rates and mechanisms controlling microbial reduction of U in heterogeneous field settings, and (2) to develop a system capable of delivering electron donor to a highly heterogeneous subsurface environment enabling spatially uniform in situ immobilization of U in groundwater upon passage through a subsurface biocurtain. This work involves a 3-phase field study in a near surface aquifer at Oak Ridge, TN. This aquifer contains very high levels of nitrate and part per million levels of U(VI). The nitrate must be removed because it prevents reduction of U, and, if the nitrate is reduced to N2 the resulting gas could reduce aquifer permeability. We will test in-situ concepts for nitrate removal: an in-well vacuum stripper; an in-well bioreactor; and ion selective resins. The most effective and least expensive system will be coupled to a system for in-situ uranium removal. By removing the nitrate, we will be able to impose hydrological and geochemical controls on the U source permitting reliable determination of U reduction rates within a downgradient biocurtain for U immobilization. We plan to use field-scale and companion bench-scale studies to evaluate hypotheses on dissimilatory metal-reducing activity, and we will be monitoring changes in microbial community dynamics using molecular methods.

- Proof of gene expression during bioaugmentation - Craig Criddle (WRHSRC, EPA) Experimental justification for bioaugmentation is typically obtained by comparing the bioremediation of inoculated and uninoculated samples. This approach is adequate for bench-scale studies. At full scale, however, design and operation of uninoculated controls is difficult and expensive. Inadvertent inoculation of "uninoculated" regions must be avoided, and the inoculated and uninoculated regions

must initially be geologically, chemically, and biologically similar. Other methods, besides the use of uninoculated control regions, are needed to establish that added organisms are in fact mediating the desired transformations. A logical approach is to prove expression of the genes required for the desired transformation. Gene expression occurs at different levels as the synthesis of mRNA (transcription), the formation of polypeptides (translation), and the biochemical reaction itself. Proof of gene expression is best obtained at each level, because each piece of evidence strengthens the conclusion that gene expression is occurring as intended. This proposal explores each level of gene expression for the bioremediation of carbon tetrachloride by Pseudomonas stutzeri KC.