National Research Program of the Water Resources Division, U.S. Geological Survey, Fiscal Year 1992

United States Geological Survey
Open-File Report
93-128

NATIONAL RESEARCH PROGRAM OF THE WATER RESOURCES DIVISION, U.S. GEOLOGICAL SURVEY, FISCAL YEAR 1992

Compiled by MARTHA L. NICHOLS and LINDA C. FRIEDMAN

U.S. GEOLOGICAL SURVEY
Open-File Report 93–128

RESTON, VIRGINIA
1993

DEPARTMENT OF THE INTERIOR
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CONTENTS

THE NATIONAL RESEARCH PROGRAM OF THE WATER RESOURCES DIVISION, U.S. GEOLOGICAL SURVEY FISCAL YEAR 1992

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INTRODUCTION

This report, one in a series of annual reports, provides current information about the National Research Program (NRP) of the U.S. Geological Survey's Water Resources Division (WRD) during fiscal year 1992. Organized by NRP's six research disciplines, the volume contains a summary of the problem, objective, approach, and progress for each project that was active during fiscal year 1992. It also contains bibliographic information that, because of the long-term nature of the program, covers a 5-year period. The bibliographic information does not include abstracts or informal reports. Rather it contains those reports that are readily available in the form of journal articles, U.S. Geological Survey (USGS) publications, book chapters, or books.

BACKGROUND

The National Research Program has been an integral part of the U.S. Geological Survey's Water Resources Division since the late 1950's. The NRP conducts basic and problem oriented research in support of the mission of the U.S. Geological Survey. Relevant hydrologic information provided by the USGS is available today to assist the Nation in solving its water problems because of a conscious decision made in years past to invest in research. The NRP is designed to encourage pursuit of a diverse agenda of research topics aimed at providing new knowledge and insights into varied and complex hydrologic processes that are not well understood. The emphasis of these research activities changes through time, reflecting the emergence of promising new areas of inquiry and the demand for new tools and techniques with which to address water-resources issues. Knowledge gained and methodologies developed in this program apply to all of the hydrologic investigations of the USGS, to the water-oriented investigations and operations of other agencies and to the general scientific community. Through the years, many of the Geological Survey's major research and resource assessment initiatives related to existing and emerging national water-resources problems have had their origins in the NRP.

Since its beginning in the late 1950's, the NRP has grown to encompass a broad spectrum of scientific investigations. The sciences of hydrology, mathematics, chemistry, physics, ecology, biology, geology, and engineering are used to gain a fundamental understanding of the processes that affect the availability, movement, and quality of the Nation's water resources.

Results of NRP's long-term research investigations often lead to the development of new concepts, techniques, and approaches that are applicable not only to the solution of current water problems but also to future issues that may affect the Nation's water resources. Basic tools of hydrology that have been developed by the NRP include ground-water modeling, geochemical modeling, and regional flood frequency analysis. These and other tools developed by the NRP are in common use today throughout the USGS, in other agencies, and in the private sector.

In consultation with NRP managers and research advisors, NRP projects set long-term research goals. Projects typically conduct research during a period of several years as studies progressively resolve questions of great complexity. In conducting such long-term efforts, most projects employ a combination of detailed field observations, laboratory experiments and analyses, and some kind of conceptual or mathematical modeling of the processes involved. Often, NRP projects cooperate with WRD District projects and other NRP projects to conduct multidisciplinary studies—combining, for example, ground-water flow with ground-water chemistry or surface-water chemistry and ecology.

ORGANIZATION OF THE NATIONAL RESEARCH PROGRAM

The NRP is located principally in Reston, Virginia; Denver, Colorado; and Menlo Park, California. A Chief, Branch of Regional Research (BRR), at each location is responsible for managing the program and serves as a liaison with the WRD's operational program. The Chief, BRR, reports directly to the Chief, Office of Hydrologic Research, who oversees the entire program. Organized into about 120 projects, it has a permanent staff of approximately 290 individuals and a nonpermanent staff that is made up primarily of university students and faculty.

For technical administration, the NRP is subdivided into six disciplines with a Research Adviser and Assistant Research Adviser assigned to each. The Research Advisers serve as a peer resource to the research projects and as a technical consultant to management. The six research disciplines, the scope of their activity, and the emphasis of current study are listed below:

(1) *Ecology.*—Concerned with biologic and microbiologic processes that affect the quality of water. To improve understanding of the biological effects of stress, hydrologic events, and climatic trends, the solute composition of and solute transport in surface and subsurface waters are investigated and studies are made of the response of organisms to environmental factors. Current investigations include studies of the influence of microbial processes on the fate of hazardous substances in ground water; the effect of geochemical processes on the transfer of hazardous substances to food chains that could include humans; the effect of hydrologic processes and associated environmental variables on the composition of benthic and pelagic communities; the use of organisms to help quantify and identify hydrologic events, such as floods or stress inputs; and the effect of microbial production and transformations of organic materials in the carbon, nitrogen, and sulfur cycles. Most studies are process-oriented and emphasize the interaction of physical and chemical aspects of hydrology with biological processes. The types of hydrologic regimes included in these

ecological investigations range from ground waters to lakes, rivers and estuaries, and from coastal wetlands to forests and deserts.

(2) *Geomorphology and sediment transport.*—Focuses on the understanding of channel morphology and erosional processes that govern the source, mobility, and deposition of sediment. Currently, research is aimed primarily at providing the capability for deterministic and stochastic modeling, modeling sediment transport in alluvial channels, and assessing the causes of changes in stream-sediment loads with time and the rates at which rivers adjust to changes in the quantity of water and sediment contributed to the channel.

(3) *Ground-water chemistry.*—Concerned with inorganic, organic, and biochemical reactions affecting natural and contaminated water in relation to mineralogic, geochemical, and hydrologic conditions in the ground-water environment. Laboratory research includes studies of the kinetics and mechanisms of electron-transfer reactions between mineral surfaces and aqueous solutions, the adsorption behavior of inorganic and organic solutes on particulate surfaces, the kinetics of silicate and carbonate mineral dissolution and crystal growth, isotopic fractionation in mineral-water-gas systems, the speciation of transuranium elements in ground water, the exchange properties of clays, and the thermodynamics of solubility and coprecipitation phenomena. Field studies involve controls of mineral-water-gas reactions in a wide variety of hydrochemical environments including shallow ground-water systems, regional aquifer systems, deep sedimentary basins and subsurface brines, geothermal systems, freshwater-saltwater interfaces, and the unsaturated zone. Studies include investigations of the degradation of organic matter and attenuation of toxic metals in environmentally stressed hydrochemical environments, relations between water quality and human health and disease, and physical and chemical processes affecting dispersion of dissolved solutes. Extensive applications of isotopic data are made to identify water sources, cross-formational leakage, water age, paleoclimatic conditions, and reactants and products in the ground-water environment. Current modeling research focuses on the speciation of metals and other dissolved solutes in natural and contaminant waters, prediction of the thermodynamic properties of mineral-water reactions in ground-water systems, including brines and other highly saline fluids, and prediction of chemical and isotopic evolution in water-rock systems, and age-dating ground water.

(4) *Ground-water hydrology.*—Focuses on developing understanding and techniques for evaluating and predicting the quantity and quality of water moving through porous and fractured media in order to effectively manage ground-water resources. Research into the role of the unsaturated zone is being conducted to provide information needed to evaluate ground-water conservation and management practices, such as artificial recharge, phreatophyte control, and the reduction of evapotranspiration. Currently, investigations of land subsidence are underway as are studies to determine how fracture zones, permeability distributions, and geothermal conditions affect, or are affected by, subsurface hydrologic processes. Comprehensive studies in borehole geophysics are being conducted to improve the resolution and effectiveness of these subsurface techniques. Efforts also are being made to develop new and to refine existing two- and three-dimensional models for use in

understanding flow and solute transport in porous media in both the saturated and unsaturated zones. Parameter-estimation techniques to enhance and assess model accuracy also are being developed.

(5) *Surface-water chemistry.*—Involves an assessment of natural and contaminant chemicals in water and sediment, as well as the study of fundamental chemical and biochemical processes that affect the movement of organic and inorganic solutes and gases through primarily surface-water systems. Projects now underway include characterization of natural and manmade organic substances, identification of organic pollutants in natural waters, interaction of trace metals and radionuclides with natural organic substances and sediments, study of biodegradation processes of organic compounds, study of climate and carbon fluxes, hydrochemistry and paleoclimatology in arid regions, investigations of nutrient and metal fluxes in natural-water systems, the study of the effect of contaminated precipitation on corrosion of building materials, and the effects of acid rain on water quality.

(6) *Surface-water hydrology.*——Stresses studies to develop understanding and techniques needed to improve the ability to predict the occurrence, distribution, movement, and quantity of the Nation's surface-water resources, and to explain quantitatively how these resources may be affected by natural or human-induced changes. Ongoing projects generally can be grouped into studies of: (a) all hydrologic processes that govern the infiltration, evapotranspiration and runoff from basins, especially as they relate to an analysis of the effect of land uses such as surface mining, agriculture, and urbanization; (b) the laws of random processes and how these laws are related to the statistics of extreme events, such as floods, droughts, or other natural hazards; the areal distribution of hydrologic information; and the accuracy and reliability of deterministic models of hydrologic systems; (c) the hydraulics or hydrodynamics of flow in single or multi-dimensional surface-water systems, and how this flow is related to the safety and welfare of people that encroach on the water body; (d) the sources, transport, and fate of constituents that are related to water quality in surface waters; and (e) the accumulation, movement, and melting of snow or ice, particularly the ways in which the presence of snow and ice affects climate, water supply, and (or) safety.

TECHNOLOGY TRANSFER

The dissemination of the new understanding and techniques that are developed by the research projects is considered an important part of the NRP. Results from NRP research studies are published in appropriate publication outlets to assure wide dissemination of research results. Outlets include refereed scientific journals and USGS Water-Supply Papers and Professional Papers. Knowledge of new techniques for hydrologic investigations, such as: sampling methods, laboratory methods, or mathematical models, and other research results is transferred to the scientific community and to the public through presentations at professional society meetings and other scientific and public gatherings as well as through publications. Furthermore, to disseminate research knowledge within and throughout the USGS, project personnel conduct appropriate USGS training courses, collaborate and advise other USGS scientists, and provide technical programmatic advice to USGS management.

This report is intended to help with technology transfer by describing the work in progress, the expertise, and most importantly the publications produced by the NRP. Readers are encouraged to seek copies of these publications from the specific NRP project that prepared them. Addresses and phone numbers of Project Chiefs are provided in the text. For the reader's convenience two appendices are provided. The first is arranged alphabetically by the name of the Project Chief and the second is arranged alphabetically by topics that we believe may be of interest.

ECOLOGY

TITLE: Interactions Between Organic Solutes and Trace Metals in Natural Waters, and Their Ecological Role (CR 84-286)

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Benjamin G. Budka, Physical Science Tech.
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PROBLEM: Aquatic humic substances and other classes of dissolved organic material in natural waters can control the biogeochemistry of trace metals and other solutes and can influence ecological processes in lakes and streams. The nature and reactivity of the dissolved organic material is, in turn, influenced by biological, chemical, and physical processes in the aquatic environment. Recent advances in isolating and characterizing different fractions of dissolved organic carbon (DOC) and in measuring rates of microbial processes can be used to advance the understanding of the dynamic relations among aquatic biota and dissolved organic material and trace metals in different environments.

OBJECTIVE: (1) Determine the processes involved in the biogeochemistry of dissolved organic material and selected trace metals in several aquatic environments; (2) describe the temporal and spatial dynamics controlling the concentration and chemical speciation of trace metals and DOC in aquatic environments; and (3) quantify carbon flux and feedback processes involving dissolved organic material in aquatic ecosystems.

APPROACH: (1) Use conventional and newly-developed methods to isolate and characterize aquatic and humic substances and other organic acids from several on-going field sites; (2) conduct potentiometric titrations and other laboratory experiments to determine the dependence of copper and iron complexation by humic substances and other organic fractions on pH and counterion complexation; (3) continue ongoing field studies of biogeochemical interactions between dissolved organic material and trace metals. Field sites include two mountain streams, several lakes in Colorado and Minnesota and a bog in Massachusetts; (4) conduct field research at lakes and streams in the Dry Valleys in Antarctica to determine the carbon cycling and phytoplankton dynamics in ecosystems with only autochthonous production by algal and microbial processes; (5) evaluate global scale interactions involving dissolved organic material and trace metals.

ECOLOGY

PROGRESS: A study of the temporal and spatial dynamics of trace metals and natural organics in a mountain stream system has shown that the photoreductive dissolution of iron oxides releases phosphate which is assimilated by periphyton. We are conducting a study of polar desert lakes and streams in Antarctica, through National Science Foundation (NSF)-Division of Polar Programs. We characterized microbially derived dissolved fulvic acids from two lakes in the Taylor Valley, Antarctica, that receive no inputs of organic material from the barren polar desert. We developed a hypothesis that these compounds are predominantly produced in the lake sediments and diffuse upward and have interpreted DOC profiles from two other lakes in this context. This season we also have obtained fulvic acids from algal rich coastal ponds in Antarctica and the results support this hypothesis. We have developed a way to evaluate DOC sources by plotting atomic C/N ratios versus the ratio of aromatic and aliphatic carbon. We have extended this approach to another humic fraction (hydrophilic acids) and to include marine samples. For the past two seasons, the Antarctic research has included measurements of streamflow and quantification of geochemical reactions in the substream zone. As a result of increasing streamflow with climate warming trends, lake levels have been rising and two lakes have merged. We have conducted a study of radionuclide transport at Rocky Flats, Colorado; preliminary results indicate that interaction with organic-rich colloids are important in transport.

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TITLE: The Role of Chemical Fluxes in the Biogeochemistry of Inland Surface Waters, Including Lakes, Reservoirs, and Wetlands (CR 85-293)

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PROBLEM: Most studies of the biogeochemistry of inland aquatic ecosystems have been confined to processes within the water body. The effect of ground-water fluxes to the water body on ecosystem biogeochemical processes has been ignored. Detailed studies of all external chemical fluxes and their relationship to the supply and loss of biologically important chemical elements are virtually nonexistent, particularly for aquatic ecosystems lacking channelized surface-water inflow and outflow. Research on these external fluxes and their quantitative significance is critical for decision makers responsible for water quality and biological productivity of lakes, reservoirs and wetlands.

OBJECTIVE: The primary objective of hydrological-biogeochemical interaction research is to understand relative contribution of all hydrologic processes controlling fluxes of biologically important chemical elements between surface waters and their watersheds. The importance of different transport pathways affecting the supply and loss of those elements from surface water will be quantified. Although this research will emphasize experimental field work, conceptual models of hydrological-biological interactions will be used to identify important mechanisms to be investigated further in the field.

APPROACH: The supply and loss of biologically important chemical elements in surface waters (lakes, reservoirs, wetlands) will be quantified by field sampling and experimental studies at existing experimental field sites that have been the subject of intensive hydrologic research including onsite measurement of the entire hydrologic cycle. Field data will be used to develop empirical models and calibrate conceptual models of hydrological-biogeochemical interactions.

PROGRESS: A report was published on the interrelation of changing hydrological conditions, chemical characteristics, and wetland vegetation at a site in the Cottonwood Lake, North Dakota, area site for the period 1967-89, with emphasis on the period of detailed study from 1979-89. A report was written on prairie pothole wetlands for USGS circular on wetlands. Intensive studies of chemical fluxes, including determination of ground water flux, and lake chemical and biological investigations, continued at Cottonwood Lake area wetlands, North Dakota; Crescent Lake National Wildlife Refuge, Nebraska; and Shingobee and Williams Lakes, Minnesota.

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TITLE: Microbial Transformation of Dissolved Organic Carbon in Aquatic Environments (CR 86-295)

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PROBLEM: Although it is recognized that micro-organisms play an important role in the transformation of organic compounds in aquatic habitats, very little is known about the exact nature of these transformations in either pristine or contaminated environments. Within the context of in situ environmental conditions, the mechanisms, pathways, rates, and factors controlling carbon cycling by micro-organisms are poorly understood; however, these particular processes can significantly affect the entire range of biogeochemical and geochemical processes occurring within the aquatic environment.

OBJECTIVE: Study the mechanisms, pathways, and rates of transformation of organic compounds (natural and contaminant) mediated by micro-organisms in aquatic habitats and identify some of the factors controlling these transformations. Examine the effect that these transformations have upon other biogeochemical processes.

APPROACH: Select a pristine alpine stream, an amictic Antarctic lake, and a sewage-contaminated aquifer as the habitats of primary focus. Determine microbial processes in both water and sediment samples by use of tracer techniques for laboratory and field studies. Develop sample-handling techniques needed to maintain in situ conditions. Employ experiments with isolated cultures of micro-organisms, when necessary, to help interpret the results obtained with natural samples.

PROGRESS: Our studies were continued to determine the nature of denitrification (microbial reduction of nitrate to nitrogen gas) in nitrate-contaminated ground water. When it occurs, this process represents a potential bioremediation mechanism to treat nitrate contamination, but it can also affect the geochemistry of an aquifer. (1) We discovered that a commonly used technique in surface soils to measure denitrification enzyme activity was unsuitable for ground-water denitrifying populations. Using a variety of approaches, it was determined that the failure was due to a previously unknown inhibition of the enzyme activity by chloramphenicol, a bacteriostatic agent added to the assay flasks to prevent new growth during the assay. The unique nature of ground-water denitrification actually facilitated this discovery and allowed us to bring it to the attention of soils scientists. (2) We also isolated and characterized several strains of autotrophic, hydrogen oxidizing, denitrifying bacteria from ground water. Although little is known about their physiological capabilities, it appears that these bacteria are commonly found in the subsurface. Our results demonstrate that they have a high affinity for hydrogen, and given that the end products are innocuous, the process appears to be suitable as a bioremediation mechanism. (3) We are continuing to develop natural gradient tracer tests as a tool to measure microbial processes in situ in ground water. These tests can determine the actual rates and kinetic parameters of a microbial process without disrupting the microbial populations within an aquifer or the hydrologic regime to which they are adapted. Two 30-day tests have been conducted to specifically quantify denitrification in nitrate-contaminated ground water and a paper is being written comparing the results of these tests with laboratory incubation techniques.

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ECOLOGY

TITLE: Ecological Interactions of Lakes and Streams (CR 88-312)

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PROBLEM: Much aquatic habitat in North America is or has been destroyed by development or by extracting natural resources. Little is known concerning the requirements for aquatic life in streams or lakes,especially from a geomorphic standpoint. In this regard, it is difficult also to separate natural from man-caused changes in aquatic ecosystems.

OBJECTIVE: To determine the effects that geomorphic and other physical as well as chemical and biological changes have on aquatic habitat and upon the distribution and abundance of aquatic organisms.

APPROACH: Several stream sites above lakes and their receiving lakes, will be selected and instrumented for flow temperature and mapped for geomorphic features. The aquatic flora and fauna will be measured. Alterations in hydrologic regime, including geomorphic changes will be made and their effect upon stream and lake organisms determined.

PROGRESS: Our work continues on streams and stream habitat in Yellowstone National Park, Wyoming. A new parkwide project on stream benthos, physical and chemical habitat was initiated in FY 1992. Work in the Catskill Mountain streams continues. Reports on work on the Colorado River are under preparation. We are working on the Denali National Park, Alaska, paper and it should have Director's approval by April 1993. The report on the firehole and Gibbon River is in first draft format.

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ECOLOGY

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TITLE: Characterization of Biotic and Biogeochemical Interactions at Environmental Interfaces (CR 91-320)

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PROBLEM: Recent increases in the atmospheric concentrations of carbon dioxide and methane have emphasized the need for a more complete understanding of the processes that control carbon transfer among air, land, and water. Knowledge of the amount, rate and chemical form of carbon transfer across environmental interfaces, such as the land-air and water-air interfaces, is of particular importance. These fluxes are commonly controlled by a combination of physical, biological, and chemical processes at or near the interface. Isolation of the primary mechanisms that determine carbon transfer across the interface allows for development of process-based models that can be used for carbon mass-transfer estimates at the ecosystem or landscape scale. This process-based knowledge is also useful for prediction of the long-term effects of land- or water-use change on carbon mass transfer rates.

OBJECTIVE: Characterize and quantify the carbon transfer that naturally occur across environmental interfaces, and isolate the physical, biological and chemical controls of those fluxes. Where possible, evaluate the effects of environmental change on the observed interactions. Develop process based models that explain field and laboratory observations.

APPROACH: Select field sites that represent a range in abiotic and biotic conditions that control carbon transfer across environmental interfaces, and systematically measure relevant control variables and fluxes. Conduct field and laboratory experiments to test hypothesized interactions. Current investigations are focused on characterization of carbon dioxide and methane transfer across land-air and water-air interfaces. Emphasis is placed on the physical and geochemical properties that control carbon dioxide and methane transport and on factors that control the production and consumption of these gases by soil- and fresh-water biota.

PROGRESS: Results of our field study of the uptake of atmospheric methane by desert soils demonstrate that arid regions are an important global soil sink for atmospheric methane, and that methane consumption in those regions can be enhanced by soil moisture increases. A generalized model of the diffusional limits on atmospheric methane consumption by soils was developed that sets limits to the rate of soil uptake of atmospheric methane based on physical conditions. Results of our study of soil respiration and atmospheric methane uptake in tallgrass prairie demonstrate that soil respiration and methane consumption increase in recently-burned versus unburned prairie. The conversion of prairie to tilled agricultural land substantially reduces the atmospheric methane sink.

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TITLE: Interdisciplinary Research Initiative (IRI) at the Shingobee Headwaters Research Area, Minnesota (CR 90-323)

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PROBLEM: Surface-water gaging structures were installed on three streams. A climate station was established to collect data on solar radiation, air temperature, wind speed and direction, and humidity. Wells and piezometers were constructed at four localities. Water samples were collected for a wide range of inorganic, organic, trace, and isotopic constituents from the atmosphere, 2 lakes, 3 streams and 15 wells. In addition, several interest groups have been established to focus interdisciplinary research on specific topics. These include: (1) A group of scientists concerned with comparing the carbon budget between Williams Lake, the lake presumably dominated by internal cycling, and Shingobee Lake, the lake presumably dominated by external fluxes. (2) A group of scientists concerned with comparing phytoplankton and zooplankton interaction in both lakes. (3) A group of scientists concerned with the interconnection between the Shingobee River, a large fen, a small lake, and an intervening narrow upland.

OBJECTIVE: The Interdisciplinary Research Initiative (IRI) was designed to focus attention on lakes and their contiguous watersheds. Lakes were selected because they are important aquatic systems that integrate a large number of processes within their watersheds, and they have great importance to society. The basic question to be addressed is based on water residence time; that is, how do lakes that have a short residence time, which usually have large streams entering and leaving them, differ from those that have a long residence time? Field experimental sites for both terrestrial and aquatic systems will be mutually selected by all interested specialists and sampled for physical, chemical, and biological characteristics so all involved will be working with a common data base, and presumably on common problems.

APPROACH: The Interdisciplinary Research Initiative was designed to focus attention on lakes and their contiguous watersheds. Lakes were selected because they are important aquatic systems that integrate a large number of processes within their watersheds, and they have great importance to society. The basic question to be addressed is based on lake water residence time; that is, how do lakes that have a short residence time because of large streams entering and leaving them, and are presumably dominated by external fluxes, differ from those that have a long residence time because they have no streams or very small streams and are presumably dominated by internal cycling. Field experiments for both terrestrial and aquatic systems will be mutually selected by all interested specialists and sampled for physical, chemical, and biological characteristics so all involved will be working with a common data base on common problems.

PROGRESS: Data collection and processing proceeded at a very efficient rate. All data on climate, surface water and ground water were processed, quality controlled, and imported to the IRI data management system.

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Sturrock, A.M., Winter, T.C., and Rosenberry, D.O., 1992, Energy-budget evaporation from Williams Lake—a closed lake in north-central Minnesota: Water Resources Research, v. 28, no. 6, p. 1605–1617.

TITLE: Limnological Phenomena in Impounded Rivers (CR 91-325)

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PROBLEM: Dams have been built in this century that impound virtually all major rivers in the United States. The purposes vary and include flood control, navigation, hydropower generation, and storage for irrigation and domestic uses. About 2,500 reservoirs of 5,000 acre-feet or more, store about 480 million acre-feet, about 1/4 of the annual runoff. Storage capacity is dominated by large reservoirs such that the 600 largest store more than 90 percent of the total. Lake Powell, behind Glen Canyon dam, stores water (about 27 million acre-feet) in the upper basin of the Colorado River for controlled release according to the Colorado River Compact (8.23 million acre-ft per year) and to generate electricity for sale to consumers in the southwestern United States (about 80 percent of the generating capacity of the Colorado River Storage Project). Phenomena that control the quantity (evaporation, losses to ground water, consumptive uses in the basin, regional drought or El Niño effects, and so forth) and (or) quality (salinity (chemistry), productivity, sediment-water column exchange, and so forth) of reservoir waters are not understood.

OBJECTIVE: General: To continue review of literature and of historic data sets, to continue field reconnaissance, and development of long-term monitoring and research with the National Park Service and the Bureau of Reclamation, the agencies with management and regulatory responsibility for Lake Powell.

Specific: To initiate investigation of basic processes that mediate water quality in Lake Powell; and, to couple understanding of processes in Lake Powell to management of water quality in the Colorado River in the Grand Canyon National Park.

APPROACH: Several approaches are being developed, led by the development of a conceptual model of reservoir patterns and the major driving processes. (1) Conduct field measurements for calibration of LANDSAT-TM images, so that the spatial variation (longitudinal gradients and lateral exchanges with tributary embayments) can be assessed in greater detail. This might lead to a history of productivity because the LANDSAT-TM covers the full-pool history of Lake Powell. (2) Examine the sediment distribution, the pore-water chemistry and the benthic community of the Colorado and San Juan deltas that represent the accumulation of materials since the construction of the dam. (3) Initiate productivity and water chemistry work in the forebay and the tailwaters to couple reservoir seasonal pattern and dam operation to biological processes in the Grand Canyon.

PROGRESS: Two reconnaissance trips to Lake Powell were completed (October 1991 and April 1992). The latter included extensive evaluation of trophic gradients combining conventional plankton sampling methods with hydroacoustic assessment of fish biomass distributions. The present low water level means that water released from the dam may come from the warm mixed layer rather than the cold deep layer some time this year. Because of this and incomplete vertical mixing during isothermy there are several chemical implications of this shift. The interim flow prescription (1991–1994) made no provision for the effects of low reservoir levels. We are watching this pattern develop. Collections of Lake Powell calcite deposits were made under the low lake level conditions. Future analysis of these collections may yield information on spatial variability of reservoir processes.

ECOLOGY

TITLE: Interaction of Bacteria with Environmental Contaminants and Solid Surfaces in the Aquatic Environment (CR 91-327 (Formerly, WR 86-191))

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PROBLEM: Although efforts have been made to explain the behavior of heavy metals and refractory organic contaminants in aquatic habitats in the framework of known geophysical and geochemical processes, much remains to be learned about the role of bacteria in such behavior. Of particular interest are bacteria-contaminant interactions in ground water. Because of the persistence of some contaminants in the subsurface environment and because of increasing demands for both high-quality ground water and on-land disposal of toxic chemicals and radioisotopes, these interactions should remain important environmental problems for the next few decades. Because significant biotransformation/biodegradation of many environmental contaminants in aquifers and particle-laden surface waters can occur at particle surfaces, explanations for bacteria-contaminant interactions in such environments should take the presence of particles into account.

OBJECTIVE: Provide some of the microbiological information necessary for realistic predictions of contaminant behavior in aquatic environments. Obtain information on specific mechanisms of interactions between environmental contaminants and aquatic bacteria, taking into account adsorption, active uptake, competition, biotransformation reactions, interaction with extracellular polymers, effects of nutrient and physicochemical gradients, and effects of particle surfaces. Investigate the effect of nutrient and physicochemical conditions on subsurface transport of bacteria (because the role of bacterial transport on the fate of environmental contaminants in ground water is unknown).

APPROACH: (1) Study the influence of solid surfaces on microbial activity and mobility in particle-laden aquatic environments, particularly freshwater aquifers; (2) study the effect of organic contaminants on the distribution, transport, and activity of the bacterial population and the nature of the microbial community in ground-water habitats; and (3) conduct flow-through column experiments to assess the role of adherent bacteria on the mobility and fate of selected inorganic and organic contaminants in simulated aquifer environments. Conduct flow-through column experiments to investigate factors affecting sorption and movement of bacteria in porous media.

PROGRESS: A survey of protozoan diversity, abundance, and distribution in organically-contaminated and uncontaminated zones of a sandy, unconfined aquifer in Cape Cod, Massachusetts, was completed (Phase 1 of a collaborative National Science Foundation grant, co-written by Dr. N. Kinner, University of New Hampshire, and Dr. C. Curds, British Museum of Natural History). Important findings of the survey included large protozoan populations (approaching 100,000 per gram of sediment) in some contaminated zones, suggesting a potentially important role in the microbial ecology and in the fate of organic compounds in contaminated ground water. Substantial populations of protozoa were also found in uncontaminated and in anoxic (dissolved oxygen-free) zones of the aquifer. A field experiment comparing the relative transport behaviors of indigenous ground-water bacteria, bacteria-sized microspheres, two well-defined viruses, and a conservative tracer was conducted collaboratively with the University of Arizona at an array of multilevel ground-water study sites. Three papers involving movement of bacteria in ground water were published. The first phase of a laboratory study assessing the role of ground water chemistry and mineralogy upon sorption of bacteria in the presence of chemically-modified and unaltered aquifer sediments from the Cape Cod site was completed.

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ECOLOGY

TITLE: Effects of Toxic Substances on Aquatic Communities (CR 92-337 (Formerly WR 75-137))

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PROBLEM: Water pollution is principally a biological problem in that its primary effect is on aquatic organisms. Yet, most pollution assessment emphasizes the measurement of chemical and physical variables rather than responses of aquatic organisms to these variables. There are several reasons for this contradictory emphasis on physiochemical variables, but perhaps the most compelling is the lack of predictive information on responses of aquatic organisms, singly or in association, to specific environmental factors. There is a need to evaluate the predictability of measurements based on such biological responses with a view towards their greater acceptance in water-quality assessment and towards development of methods for objectively defining relationships among biological and physiochemical variables in aquatic ecosystems.

OBJECTIVE: Determine through detailed studies of organisms, simplified ecosystems, and natural sites, the extent to which waterborne contaminants and (or) disturbance affect the production and structure of aquatic plant assemblages and the growth and reproductive capacity of aquatic animals. Evaluate methods assessing effects of chronic exposure ot contaminants and (or) disturbances on individual species and natural aquatic communities.

APPROACH: Evaluate methods for assessing effects of waterborne contaminants released to the environment, including tests of embryogenesis and growth in fishes, survival of critical life stages of aquatic invertebrates, and population growth rate of algae. Determine physiochemical factors affecting responses and bioaccumulation of these contaminants. Evaluate methods and results of laboratory studies by field experiments. Determine the utility of biological test methods for detecting and monitoring environmental concentrations of toxicants. Examine the factors (physiochemical and biological) influencing responses of natural aquatic communities.

PROGRESS: One of the primary objectives of the ecological survey element of the National Water Quality-Assessment (NAWQA) program is to develop an improved understanding of the interrelation of upland, riparian and in-stream physical characteristics, stream chemistry, and the composition and function of biological communities. This project has been working in support of that objective.

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ECOLOGY

TITLE: Remote Sensing and Ecological Research in Wetlands (NR 73-090)

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PROBLEM: Wetlands are hydrologically controlled ecosystems essential to estuarine, marine, lacustrine, and riverine productivity. To improve our understanding of these ecosystems we need information on (1) wetland hydrologic variables/budgets and their relation to wetland vegetation and nutrient cycling; (2) wetland dynamics and boundary fluctuations; (3) wetland functions and values; and (4) short- and long-term temporal changes. Wetland plants may serve as sensitive hydrologic indicators of water-quality parameters such as salinity, turbidity, pH, nutrients; presence of various pollutants; or frequency and duration of inundation. Submersed aquatic wetlands have many functional functions including (1) habitat for invertebrate species; (2) food and (or) shelter for juvenile and adult fish, waterfowl, and other wildlife; (3) retarding flow velocities, stabilizing bottom sediments, and slowing erosion; and (4) oxygenating the water, recycling or transforming nutrients and heavy metals. Decline or disappearance of aquatic plant communities or overgrowth of submersed vegetation under nutrient- enriched conditions is of concern to scientists, ecologists, environmentalists, and managers. The factors affecting distribution and abundance of submersed aquatic vegetation and the effect of submersed aquatic vegetation on water quality are poorly understood.

OBJECTIVE: (1) Determine factors responsible for the changing distribution of submersed macrophyte beds in the tidal Potomac River and other lacustrine and riverine environments; (2) study processes controlling the survival, expansion, and decline of macrophyte populations; (3) determine the effect of submersed macrophytes on water velocity, water quality, and carbon flux; (4) characterize wetland transition zones and relate distribution of vegetation to soils, hydrology and elevation; (5) examine seasonal and long-term changes in wetland ecology as related to changes in environmental parameters including hydrology, water quality and land use; and (6) aid in the development of models that utilize sensing biological and hydrologic remote sensing wetland data as part of their primary data base.

APPROACH: (1) Conduct field and laboratory investigations of the factors affecting survival and growth of submerged aquatic plants, (2) conduct field and laboratory experiments to measure productivity and to determine the effect of submersed macrophytes on water quality and carbon flux, (3) develop models illustrating relationships between plant success and other environmental factors, (4) conduct studies on the hydrology and ecology of selected wetlands in the local area, at the Shingobee-Williams Lake Watershed in Minnesota, and at the Water, Energy, and Biogeochemical Budgets (WEBB) program site in Wisconsin.

PROGRESS: Laboratory studies were conducted comparing the growth of *H. verticillata* and *V. americana* under different conditions of light and temperature. *H. verticillata* has relatively small tubers compared to *V. americana* and thus has smaller reserves to draw upon in the spring. Our results showed that the recumbent growth habit of *H. verticillata* put it at the disadvantage compared with *V. americana* under poor spring light conditions. This may partially account for the 1989 decline in *H. verticillata* in the tidal Potomac River and the failure of revegetation in subsequent years.

Biomass and species composition of submersed macrophytes in Shingobee and Williams Lakes in Minnesota were sampled by diver during August 1991. The floating-leaf zone of Shingobee Lake was dominated by *Nymphaea/Nuphar* and *Ceratophyllum demersum*, and the open water zone was dominated by *Ceratophyllum demersum*. The floating-leaf zone of Williams was dominated by *Nymphaea/Nuphar*, *Najas flexilis*, and *Myriophyllum exalbescens*, and the open-water zone was dominated by *Myriophyllum exalbescens* and *Potamogeton amplifolius*. Vegetation was generally sparse in both lakes at depths greater than 4 m. *Utricularia vulgaris* and *Potamogeton richardsonii* were found only in Shingobee Lake and *Nitella* sp., *Bidens beckii*, several *Potamogeton* spp., and *Sagattaria graminifolius* were found only in Williams Lake. These macrophytes are an important component of the nutrient cycles in lakes.

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TITLE: Modeling of Microbially Catalyzed Geochemical Reactions in Aquatic Environments (NR 87-136)

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PROBLEM: Micro-organisms catalyze most of the natural redox reactions involving carbon, sulfur, nitrogen, and metals. Thus, geochemical models of the distribution and fate of natural and contaminant compounds must include a microbiological component, which requires an understanding of the physiological characteristics of micro-organisms that control the rate and extent of microbially catalyzed reactions.

OBJECTIVE: (1) Quantify the rates of microbial process that influence the geochemistry of surface water and ground water; (2) determine the physiological characteristics that control the rate and extent of microbial processes; and (3) develop mathematical models of the distribution of microbial processes in surface water and ground water.

APPROACH: Quantify rates and pathways of microbial processes with radiotracer, stable-isotope and inhibitor techniques. Determine microbial physiological characteristics with experimental manipulations of natural, mixed populations and pure cultures. Combine data on physiological characteristics with appropriate geochemical models to generate models for the distribution of microbial processes.

PROGRESS: Discovered that our previous discovery of microbial enzymatic uranium reduction could be used to effectively precipitate uranium from solution. This metabolism was used to remove uranium from a variety of real-world contaminated surface and ground waters. Various treatment systems that were highly effective on the bench- scale were developed. Several new uranium-reducing micro-organisms were discovered. An application for a patent for this process was filed. This process was the subject of over 40 stories in the media during the last year.

The uranium reductase was purified from *Desulfovibrio vulgaris*. This represents the first isolation of a dissimilatory metal reductase, and hence has important implications for understanding how micro-organisms reduce metals in general. Furthermore, the isolation of a uranium-reducing enzyme has important practical applications. With knowledge of the enzyme involved in uranium reduction, there is the potential to over express this enzyme in various micro-organisms using molecular techniques. Also, cell-free, fixed-enzyme systems can be developed for treatment of uranium contamination.

Continued studies on microbial consumption of chlorofluorocarbon (CFC)-11 and CFC-12 confirmed that micro-organisms in a wide variety of anaerobic sediments can consume atmospheric levels of CFC-11 and CFC-12. There was no uptake by aerobic soils. CFC-11 uptake proceeded by both enzymatic and nonenzymatic mechanisms. CFC-12 uptake required active microbial metabolism. A defined system containing hematin was found to serve as a model for the nonenzymatic uptake of CFC-11. *Clostridium pasteuranium* was found to provide a model for the uptake of CFC-12 during active microbial metabolism. This metabolism is considered to have implications for the use of CFC-11 and CFC-12 as tracers in anaerobic waters. It may also prevent some of the CFC-11 and CFC-12 buried in landfills from reaching the atmosphere. It also may provide a mechanism for destroying CFC stocks. Furthermore, even though the rates of uptake from the atmosphere are much lower than current rates of anthropogenic release, the uptake of CFC-11 and CFC-12 could have an important long-term effect on the tropospheric lifetime of these compounds. This discovery has received wide spread international media coverage.

It was discovered that the metal-reducing micro-organism, strain GS-15, represents a novel genera of micro-organisms. These analyses indicated that GS-15 is most closely related to the sulfate-reducing micro-organisms, which has important evolutionary implications. In addition to its unique metabolism, this organism was also found to have unique lipids and a c-type cytochrome that is involved in metal reduction. The name *Geobacter metallireducens* has been proposed for this organism.

The first Fe(III)-reducing micro-organism from an estuarine environment was isolated and characterized. This organism, designated strain BrY, represents only the third micro-organism known to obtain energy for growth by coupling the oxidation of organic compounds to the reduction of Fe(III). Its novel metabolism provides a model for important aspects of metal biogeochemistry in estuarine sediments.

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ECOLOGY

TITLE: Vegetation and Hydrogeomorphic Relations (NR 90–145)

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PROBLEM: Many hydrogeomorphic processes are poorly understood. Botanical evidence studies can improve flood or debris flow prediction for streams with short or no gaging-station records. Improvement of our understanding of the relation among fluvial geomorphology, sedimentation, mass wasting, plant chemistry, and plant ecology will provide insight into such problems as assessment of water quality, wetland loss, long-term effects of climatic variation, and the frequency and magnitude of destructive hydrogeomorphic phenomena. Botanical and geomorphic analyses may provide substantial information about variable source areas of runoff production and ground-water recharge.

OBJECTIVE: (1) Continue development of the combined use of botanical evidence and maximum likelihood estimators in flood-frequency prediction; (2) conduct basic research in the analysis and interpretation of the role of vegetation in natural and disturbed fluvial systems, including riparian and wetlands systems; (3) conduct basic research in the hydrogeomorphic-plant ecological aspects of watershed dynamics, including the delineation of variable source areas of runoff production and ground-water recharge, and analyses of nonpoint source pollution and basic plant- landform relations, and (4) conduct basic research into tree-ring chemistry as an indication of ground and surface water quality.

APPROACH: The approach is broadly interdisciplinary, employing techniques from the hydrologic, geomorphic, chemical and ecologic sciences. Dendrogeomorphic (tree-ring landform analyses), hydrologic (stream flow modeling, step-backwater analyses), and statistical (maximum likelihood estimator, time series) techniques are used in the paleohydrologic (floods, debris flows, landsliding) aspects of the project. The above techniques are combined with plant ecological analyses (plot and plotless sampling, species/landform mapping, multivariate biostatistical analyses), geomorphic analyses, and sedimentologic analyses to accomplish objectives 2 and 3. Objective 4 is accomplished by investigating the relationship between pollutants in water and sediments, and subsequent levels in plant tissues.

PROGRESS: Hupp and Yanosky continued and expanded a study, in cooperation with the University of North Carolina, along the Cape Fear Estuary to document and interpret the spatial and temporal patterns of saltwater intrusion and global sea level rise using element analyses of wood tissue from cypress trees growing along a saline gradient. Initial results show that the element analysis of chloride concentrations in tree rings provide spatial and temporal details of saltwater intrusion along the southern Atlantic and Gulf Coasts heretofore unavailable. The techniques used will allow for the development of predictive models that will be useful in long-term planning in these areas. A report has received Director's approval, but has not yet been submitted to a journal.

A continuing study, began in 1990, along the Chickahominy River, Virginia, has shown that riverine wetlands can remove more than 60 percent of the suspended sediments and nonpoint source pollutants (heavy metals, nutrients, organic compounds) between the headwaters near Richmond and the reservoir for Newport News, a reach about 42 river-miles long. Additionally, Yanosky's work on heavy metal analysis in wood tissue has shown that the volume and timing of transport of these pollutants can sometimes be estimated. This research project is in cooperation with the Virginia office and at least two other NRP projects. We feel confident that over the next few years our efforts will yield important insight and information on the sediment/pollutant trapping nature of riverine wetlands, their biogeochemical budgets, and the greater role of wetlands in water-quality maintenance. A paper received Director's approval and was submitted to the journal wetlands.

In cooperation with the Tennessee District and the U.S. Environmental Protection Agency (EPA) our project has studied the off-site movement of ground-water contamination from a creosote production site (an EPA superfund project), through the element analysis of wood. Also in Tennessee, a dendrogeomorphic investigation, now mostly completed (except for completion of journal articles) has shown that channelization exerts a stronger control on forested wetland sedimentation than bridge construction or most agricultural activity. This research has led to considerable insight on the poorly understood temporal and spatial patterns of sediment deposition in wetlands, wetland hydrology, and its effects on wetland-forest ecology; dendrogeomorphic techniques provide information heretofore unavailable.

Yanosky worked with King Huber, Geological Division, Menlo Park, to determine the age of a large landslide in Yosemite National Park. A report has recently received Director's approval and was submitted to the Bulletin of the Seismological Society of America.

Yanosky initiated an investigation of nickel concentrations in trees growing over nickel-contaminated aquifers at a hazardous waste site at the Aberdeen Proving Ground, Maryland, and at a stainless-steel manufacturing plant in northeastern Baltimore. A report (with

Don Vroblesky, Water Resources Division, Columbia) was recently accepted for publication by Water Resources Research.

We are involved in several other smaller or beginning projects in Virginia, Maryland, Colorado, Minnesota (IRI), South Carolina, Rhode Island, and Lousiana concerned with wetlands and (or) fluvial geomorphology and vegetation process and form using dendrogeomorphic, plant ecological, and trace element analyses.

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TITLE: Limnology: Controls on Distribution and Composition of Benthic Communities of Inland Aquatic Ecosystems (WR 61-012)

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PROBLEM: Benthic invertebrates are the aquatic organisms most widely used as indicators of stream quality. Although many factors are known to affect the abundance and distribution of species, it is usually not possible to predict changes in benthic communities caused by a given environmental perturbation. Improved understanding is needed of factors that control temporal and spatial distribution, abundance, and species composition of benthic-invertebrate associations in different types of streams. In particular, greater knowledge of the functional relations between benthic invertebrates and other components of stream ecosystems is required.

OBJECTIVE: Study the organization and dynamics of benthic-invertebrate species associations in streams. Study the relationships between environmental factors in streams--such as water and sediment chemistry, detritus, biotic interactions, and instream physical conditions--to the macroscale, mesoscale, and microscale distribution and the composition of biotic communities in streams.

APPROACH: Sample benthic invertebrates in a variety of small to large streams and relate their spatial and temporal distribution and species composition to environmental differences by use of multivariate analysis. Test relations derived from field studies in field and laboratory experiments.

PROGRESS: Completed the first quality assurance/quality control (QA/QC) analysis for invertebrate samples collected during a National Water Quality-Assessment (NAWQA) ecological survey: Illinois River 1989-1990. Results indicated sample preservative leakage was a problem and contractors made fewer errors of identification with the common species in samples versus difficult groups of species such as Acari, worms, and midge larvae. Completed design for two biology QA/QC laboratories in Denver, Colorado, one for 1993 and a new version tentatively scheduled for 1996 or 1997. Experiments with different mesh nets in drift of benthic invertebrates in small streams showed that early instar midge (*Chironomidae: Diptera*) larvae reacted differently to light than did later instar larvae. First and second instar larvae (younger) were positively phototactic and third and fourth instar larvae (older) were negatively phototactic. Data from acid streams indicated that possibly owing to lack of competition within the benthic community, species that were rare in nearby neutral streams became dominants in the acid streams. In these streams the organic detritus fraction of drift-net samples was especially abundant at daybreak and nightfall.

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TITLE: Geochemistry of Riverine and Estuarine Waters (WR 68-046)

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PROBLEM: The physical and chemical variability in our riverine/estuarine system is large, but causes and interactions are not clearly defined. Weather and climate forced variations appear to be very important, but we don't yet understand how riverine-estuarine operate on very short and moderately long time scales. Furthermore, whether they are compounded by anthropogenic impacts is not well known, but may have important consequences. Without such information we cannot understand and predict how these systems respond to variations in climate and human activities including changes in the amount, character, and timing of freshwater, toxic-waste, sediment and plant-nutrient inflows to these environments.

OBJECTIVE: To better understand the variability of the physics (circulation) and chemistry (primarily oxygen, carbon, silicon, nitrogen and phosphorous dynamics) in riverine and estuarine environments. Furthermore, to discriminate between natural variations due to atmospheric/oceanic forcing and human-caused impacts.

APPROACH: Defining temporal/spatial variability in riverine/estuarine systems is largely observational, using shipboard and in situ instrumentation as well as large meteorological/hydrological/oceanographical data bases. Analysis methods include statistical and numerical simulation models of physical, chemical and biological processes influencing these systems over a broad spectrum of space and time scales. Major estuaries, such as San Francisco Bay, will be used as a model for understanding and comparing behavior in others. Regional watershed variability will be interpreted vis-a-vis large scale regional-atmospheric and global-atmospheric and oceanic conditions including circulation, temperature, and precipitation. Intermediate linkage to watershed hydrology will be incorporated.

PROGRESS: (1) Understanding the nature and causes of salinity variability in the San Francisco Bay is important for a variety of reasons including that the delta is a source of fresh water for 20 million people. Although much of the subtidal to geologic time-scale response characteristics of San Francisco Bay are poorly understood, it is satisfying that linear time series models and dynamic models of the Bay's water circulation and mixing appear to adequately describe salinity variability over monthly to interannual time scales near the mouth. Here the mean-monthly variations in salinity with delta flow are near-linear (over the observed range in salinity flows 1922 to present). Response characteristics on daily time scales are also being studied. For example, a salinity perturbation in the coastal ocean takes roughly 50 days to travel from the Golden Gate to the Delta (with about half it's coastal ocean amplitude at Martinez in Carquenez Straits). Preliminary simulations of geologic (changing sea level) effects are not always intuitive. For example, a decrease in salinity in the South Bay might be anticipated with decreasing sea level, but the simulated response is the reverse, or an increase in salinity presumably because of the increasing effects of evaporation (on a smaller water volume). (2) Nutrient dynamics in the Bay have been shifting over annual to decadal time scales, depending on location. Over the last 3 decades the South Bay dissolved nitrogen distributions/species appear to change (improve) from a frequent suboxic environment to ammonium to nitrate-dominated forms of dissolved inorganic nitrogen, apparently in response to the increased levels of waste treatment. In the North Bay, the 1987–1992 drought response continues, with high summer values of dissolved silica (low phytoplankton removal), but the probable response for late summer/fall 1992 is not yet clear (for example, will the North Bay change from a low to high net nutrient-uptake mode?)

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TITLE: Fate of Organic Chemicals in Subsurface Environments (WR 71-068)

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PROBLEM: Release of various synthetic organic compounds to the environment has caused soil and ground-water pollution in many places. The processes that control the persistence and movement of these compounds are not well understood. A better understanding is necessary to aid in construction of models to predict movement and fate of pollutants in the subsurface and for design of control and abatement techniques.

OBJECTIVE: (1) Determine the transformation pathways of selected organic compounds by means of a combination of field observations and laboratory simulations of environmental conditions; (2) assess the relative importance of physical, chemical, and biochemical processes in the transformation of these compounds under ambient conditions; and (3) study relevant biotransformation processes in the subsurface.

APPROACH: Select one or more field sites where ground water has become contaminated with organic compounds. Collect and analyze water samples to discover the chemical transformations that are occurring in the subsurface environment. Use laboratory-simulation studies to elucidate the controls on these transformations.

PROGRESS: The project consists of field and laboratory studies of creosote contaminated ground water at the Survey's Hazardous Waste Site at Pensacola, Florida, and a new U.S. Environmental Protection Agency Super Fund Site at Jackson, Tennessee, with the aim of elucidating the various microbial and physical processes, and factors which influence them, affecting separate groups of water soluble creosote derived compounds during down gradient travel in the aquifer. Determination of the kinetics and transformation pathways of the major aromatic biodegradable components of the water soluble fraction of creosote (WSF) using single compounds as carbon and energy sources under aerobic, sulfate reducing and denitrifying conditions are being investigated. The kinetics of biodegradation of the WSF compounds under methanogenic conditions has been completed. Laboratory columns have been developed and the abiotic factors that affect movement of the major components of the WSF during down gradient travel with the ground water have been determined. A solute transport model utilizing the laboratory determined Monod kinetic parameters and sorption characteristics has been developed. The one-dimensional steady-state model has successfully modeled the transport of phenol, 2-, 3-, and 4-methylphenol in the aquifer at the Pensacola study site.

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TITLE: Availability of Trace Elements in Sediments to Aquatic Organisms (WR 75-125)

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PROBLEM: Concentrations of potentially toxic elements in sediments are orders of magnitude higher than concentrations of these elements in water. The ability of the aquatic environment to assimilate many toxic wastes depends upon how available this concentrated sediment-bound pool of elements is to aquatic organisms. Development of realistic pollution regulations, in turn, depends on prediction of assimilation capacities. Assessment of biological-indicator data for mineral exploration and pollution assessment also depend upon the understanding of factors affecting the biological availability of trace elements bound to sediments. It is established that the same biota in different environments may differ widely in their susceptibility or their response to trace elements, and that these differences may be at least partly related to the differences in the availability of metals in sediments; however, little is known about the geochemical and physiological factors that influence the transport of metals from sediments to organisms.

OBJECTIVE: (1) Study the partitioning of trace metals among the components of sediments and identify the processes that control partitioning; (2) study the influence of geochemical partitioning of trace metals in sediments on metal uptake by and effects of metals in organisms that contact sediments directly; (3) study physiological characteristics of aquatic organisms that uptake metal; (4) improve methodology that makes use of biota and sediments as indicators of geochemical conditions; (5) develop indices or models for predicting the bioavailability of metals after their release to the aquatic environment; and (6) develop methods for assessing the presence of biological effects from toxic wastes in aquatic communities in nature.

APPROACH: (1) Collect organisms and sediments from rivers, lakes, or estuaries across spatial or temporal gradients of physicochemical conditions; analyze geochemical partitioning through the use of chemical extractions, mathematical models, and statistics; and statistically assess relation of metal concentrations in organisms to aspects of the specific geochemical gradient under study. (2) Use laboratory studies on metal burdens in animals to assess biological influences such as animal size, intraspecific differences in metal tolerance, and physiological controls on metal uptake and metabolism. (3) Geochemically modify sediments or use well-defined model sediments in laboratory studies of metal uptake by organisms to identify physicochemical factors that affect metal availability and to test models derived from field studies.

PROGRESS: Completed third year of year-to-year variability study in contaminated segment of Clark Fork River. Developing joint project with the Montana District to study long-term changes in this river as remediation occurs at a U.S. Environmental Protection Agency (EPA) "Superfund" site. Conducted extensive analyses for Yakima River National Water-Quality Assessment (NAWQA) pilot study and are aiding interpretation of that data. Uncovered surprising Se contamination in watershed. Completed studies *hydropsychid caddisflies* as freshwater bioindicator species, showing that downstream trends in metal concentrations in four species of *hydropsychid caddisflies* differ at genus level and above, but much less so at the species level. Continued assessment of metal contamination in North San Francisco Bay. Clams from the most contaminated populations continue to be in poorer condition than uncontaminated counterparts and do not show seasonal shifts in condition typical of reproducing uncontaminated populations. Differences in Cd and Cu concentrations in two species of clams, where they co-occur, cannot be explained by kinetics of metal bioconcentration from solution in lab studies. Laboratory studies also demonstrate that Cd is very efficiently assimilated from algal food sources by several bivalve species; food may dominate as source of this element to food webs. Assimilation of Ag varies widely. Assimilation of Cr is determined by particle type (Cr is unavailable for assimilation when bound to iron oxides) and by degree of intracellular digestion employed by consumer. Food is an unimportant source of Cr when the metal is bound inorganically, but could dominate Cr uptake if the metal is taken up by bacteria, algae or bacterial exopolymer and passed on to the food web. Core materials indicate mixing of sediments to at least 50 cm is common in San Francisco Bay. History of anthropogenic Pb, Cu and Ag deposition is evident in Bay sediments. High levels of Cr, Ni, and V are of natural origin. Metal deposition is detectable in Tomales Bay cores, but low overall concentrations are reflective of winds from uncontaminated offshore areas.

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TITLE: Biotic Response to Climatic Variability and Human Impacts in Arid Lands (WR 76–145)

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PROBLEM: Biotic responses to climatic change or human manipulation are inherently complex because of wide differences in organism sensitivities and response times, the influence of history and scale, and the various interactions between organisms and with the physical system. In arid and semiarid lands, which cover about 12.5 percent of the Earth's land surface, the effects of climatic variability on vegetation are greatly magnified, particularly because most plants exist near their physiological limits. How arid land vegetation might in turn affect climate is uncertain, though there is some indication that decreasing cover and increasing albedo could promote regional drought. Whether in response to projected Greenhouse climates or intensified land use, vegetation in such critical watersheds as the Rio Grande and Colorado River basins is apt to change in the near future. There is a need to understand the direction and rate of this change and how it might affect water use and availability in the region.

OBJECTIVE: To achieve a dynamic understanding of vegetation change and its relation to water resources; to develop such an understanding in a manner appropriate to the hierarchy of spatial and temporal scales implicit in a study of global change; and determine whether responses of dryland vegetation to global change are predictable from the past and present behavior of vegetation?

APPROACH: The primary task of the project is to document vegetation and hydrological responses to climate variability on millennial to decadal time scales. The research entails monitoring of vegetation plots, analysis of instrumental records, and development of proxy data for times and places where direct measurements are unavailable. Plant demographic data will be collected to test hypotheses about short-term (decadal) vegetation responses to climatic variability in the 20th century. Paleoclimatological data will be developed for the southwestern region for the past 40,000 years. These data can be used to illustrate the influence of climatic change on arid ecosystems; to anticipate how these ecosystems are apt to change in the future; and to test and validate outputs from global circulation models.

ECOLOGY

PROGRESS: Whether or not terrestrial vegetation is a net source or sink of atmospheric CO_2 continues to foil attempts to balance annual fluxes in the global carbon budget. Ignored in such budgeting is tropical biomass burning, which emits 2-4 Gt of carbon per year, nearly comparable to the 5.3 Gt emitted annually by fossil fuel combustion. Unlike fossil fuel combustion, however, biomass burning in the tropics varies greatly from year to year and thus can influence interannual fluxes in atmospheric CO_2. Greater atmospheric CO_2 during El Niño years, when the tropics tend to dry globally, was attributed previously to losses in net productivity and reduced drawdown potential of tropical forests. We now suggest that El Niño-related drought also encourages substantially more agricultural burning in the tropics. Biomass burning is now being considered in atmospheric transport models to explore potential effects on the seasonal, interannual and latitudinal distribution of atmospheric CO_2.

Climatic forcing of vegetation change has been considered for both deglaciation and future greenhouse climates, usually to the exclusion of direct physiological responses to CO_2 enrichment. Trends in stomatal densities and carbon isotopes from fossil leaves spanning the last 40,000 years suggest vegetation responses to a 40-percent increase in atmospheric CO_2 at the end of the last glacial period. The competitive outcomes of differential responses (for example, C3 versus C4 plants) to such forcing could have yielded significant vegetation changes whatever the climate.

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TITLE: Plankton Dynamics in Tidal Estuaries (WR 79-164)

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PROBLEM: Phytoplankton photosynthesis is the ultimate engine that drives many biogeochemical and ecological processes in lakes, estuaries, and the ocean. For example, dynamic changes in pH, trace metal speciation, and concentrations of dissolved gases (oxygen, carbon dioxide, methane), inorganic nutrients (nitrate, phosphate, silicate), and organic compounds (amino acids, organosulfur compounds) are closely associated with fluctuations in phytoplankton photosynthesis. Trophic linkages also exist, between the phytoplankton as primary producers and populations of consumer organisms including bacteria, zooplankton, benthic invertebrates, and fish. Our scientific understanding of lakes and estuaries as dynamic ecosystems is therefore dependent upon a mechanistic understanding of both natural and human-induced variability of phytoplankton abundance, community composition, productivity, and connections to geochemical processes and other biological communities. These topics are central to poorly resolved issues such as: the growing worldwide incidence of toxic algal blooms and associated fish mortality; coastal eutrophication and increasing frequency and extent of hypoxia or anoxia; long-term and cyclic changes in fish stocks; the global significance of phytoplankton to the cycling of key elements such as C and N; and ecosystem-scale responses to both species extinctions and introductions of exotic species.

OBJECTIVE: (1) Study the distribution, abundance, species composition, and productivity of planktonic microalgae, animals, and bacteria in estuaries; (2) define and quantify processes that regulate population dynamics and productivity of planktonic organisms in estuaries; (3) define and quantify processes through which the plankton alter and reflect water quality in estuaries; (4) define and quantify benthic processes that affect plankton dynamics and productivity of estuaries; and (5) define anthropogenic impacts on estuarine ecosystems.

APPROACH: Integrate descriptive and experimental field studies and develop simulation models. Field studies indicate important mechanisms that must be taken into account in models and provide a data base for model calibration and subsequent verification. Conversely, evolving ecological models indicate processes and environmental factors that deserve particular emphasis by field studies. Feedback between model development and fieldwork will accelerate understanding of the natural system and should produce ecological models having sufficient realism to predict gross effects of human-induced perturbations.

PROGRESS: Field activities focused on: (1) background hydrographic measurements in San Francisco Bay as part of a multidisciplinary research program, including the Surface Water Toxics Program on San Francisco Bay. [Background measurements are made along a 150-km transect from the lower Sacramento River, along North San Francisco Bay, and through South San Francisco Bay to San Jose, California; sampling frequency is approximately monthly; measurements include salinity, temperature, nutrients, turbidity and suspended sediment concentrations, and phytoplankton biomass. This program has been run continuously since 1977, and is one of the longest sustained estuarine measurement programs in North America.]. (2) An intensive, multidisciplinary and multi-institutional study was continued to measure ecological and biogeochemical responses to the spring phytoplankton bloom in South San Francisco Bay. [This component included collaboration with researchers from National Aeronautics and Space Administration (NASA)-Ames, University of Tennessee, San Francisco State University, and other Survey projects. Topics included phytoplankton-bacterial coupling, use of stable isotopes (C, N) and lipid biomarkers to characterize sources of organic matter ("food") that support populations of consumer organisms and phytoplankton-nutrient dynamics.]. (3) Special investigations focused on strong wind events in 1991 in which intense resuspension elevated suspended sediment concentrations and suppressed the spring phytoplankton bloom. (4) The first year of field measurements was completed by J. Caffrey, National Research Council (NRC) Postdoctoral Associate who is measuring fluxes of inorganic nitrogen between the sediments and water column at fixed sites in South San Francisco Bay. [This is the first comprehensive annual study of any aspect of N cycling in San Francisco Bay sediments]. Papers were published on the following: (1) seasonal changes in phytoplankton patchiness in temperate zone lakes (from work conducted at the USGS Water Resources Division Interdisciplinary Research Initiative Site) including documentation of extreme patchiness under winter ice cover; (2) use of a recirculating flume to measure phytoplankton consumption by benthic invertebrates in tidal estuaries; and (3) reduced phytoplankton abundance and production in upper San Francisco Bay following the invasion and colonization of the estuary by an exotic clam species, *Potamocorbula amurensis* (an ecological equivalent of the zebra mussel). New papers were written and prepared for publication on (1) construction of a carbon budget for San Francisco Bay (a collaboration with A. Jassby, University of California-Davis); and (2) refinement of a vertical 1-dimensional model of turbulent mixing and phytoplankton population growth (a collaboration with J. Koseff and others at Stanford). Project personnel devoted considerable time and energy to the 11th International Estuarine Research Federation Meeting held in San Francisco November 1991 and attended by over 700 participants. T. Powell served as Chair of the National Science Foundation Global Ecosystem Dynamics Program (NSF GLOBEC), which will fund $7 million of research on coupled physical-biological oceanography.

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TITLE: Microbial Biogeochemistry of Aquatic Environments (WR 81-174)

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PROBLEM: Micro-organisms alter the chemistry and productivity of aquatic environments by performing complex transformations of organic and inorganic molecules. In many cases, microbes can affect the speciation, mobility, bioavailability, and toxicity of toxic elements, such as Se, Hg, and As. The mechanisms by which these reactions proceed, the in situ rates of the transformation, their quantitative significance to element cycling, the responsible micro-organisms and their physiology are poorly understood.

OBJECTIVE: Develop conceptual models of biogeochemical transformations by combining lab and field experimental work. Focus lab work on identification of biochemical pathways, and on isolation and physiological characterization of relevant microbes. Measure in situ rates of transformations, based on methods developed in the lab. Quantify physical exchanges between components, such as the flux of biogenic gases between the atmosphere and water or soil.

APPROACH: Microbial pathways will be studied in the lab using materials from various field locations. Biochemical experiments will be performed on isolated cultures of important micro-organisms. The findings from these investigations will guide the methodology employed in field work to assess in situ rates of these transformations as well as physical exchange (flux) of important materials (for example, reduced gases) between components.

PROGRESS: (1) Nitrate was shown to inhibit selenate respiration in pure cultures. (2) Two novel inhibitions of methanotrophic bacteria were discovered and employed to demonstrate their importance in governing the release of methane to the atmosphere. (3) The 10th International Symposium on Environmental Biogeochemistry was organized, chaired and successfully ran. (Theme: Global Change and the Biogeochemistry of Radiative Trace Gases.) (4) A book on the symposium is being edited by R. Oremland for publication.

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TITLE: Biotic Interface with Fluvial Transport: Processes Associated with Dissolved Solutes in Transport (WR 84-186)

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PROBLEM: Biogeochemical processes associated with the microbial community (algae, bacteria, fungi) constitute the interface between solute transport and biotic production in riverine environments. Identifying and estimating the role of biotic processes such as nitrification and denitrification by bacteria, nutrient uptake and production by epilithic algal films and decomposition of particulate and dissolved organic matter, as well as abiotic processes such absorption, are important for understanding the linkage between terrestrial, riparian, hyporheic and in-channel contributions to the nutrient chemistry of a drainage network. Relative biotic response to solutes in transport between pristine and anthropogenically modified riverine environments is poorly understood, but necessary for long-term management of surface waters.

OBJECTIVE: Identify and determine rates of biotic transformations of transported solutes at chemical-biotic interfaces in fluvial environments, including seepage areas, riparian zones, sediment/surface-water interfaces, intragravel-subsurface flow interfaces (hyporhic zone) and floodplains.

APPROACH: Laboratory experiments using communities collected from small to large streams and in situ field experiments are used to estimate biotic transformation of dissolved solutes. Field experiments are conducted at background concentrations and with mixtures of conservative and nonconservative solutes injected into both pristine and man-impacted fluvial environments. Cycling of elements which have high assimilative demand and (or) are subsequently passed to higher trophic levels are emphasized (that is, C, N, P).

PROGRESS: A comparative study of dissolved inorganic nitrogen cycling (DIN) in two pristine lowland streams in Costa Rica was undertaken with partial funding from the National Science Foundation. One stream (Salto Creek) was naturally enriched with soluble reactive phosphate (SRP) of volcanic origin, while an unenriched tributary (Pantano Creek) had extremely low background concentration. Separate ammonium and nitrate amendments to each stream (with rhodamine WT as a conservative tracer) indicated high nitrification potential and retention of amended ammonium, and some net nitrate production during nitrate amendment in both streams. SRP concentrations were unaffected by either amendment. SRP concentration in the unenriched stream appeared to be controlled by abiotic exchange between sediment and channel water whereas SRP in the naturally enriched stream is controlled by the volcanic inputs (work with C.M. Pringle, Cornell University, and G. Zellweger, WRD, Menlo Park). A nitrate-chloride enrichment experiment was also conducted under high-flow conditions at the Shingobee River, Minnesota (WRD Integrated Research Inititative Site). Some transient storage of solutes was observed, presumably associated with macrophyte beds growing in the sand bed-channel. Cross sectional area for storage was 10 to 20 percent of total cross sectional area (hyporheic plus channel). Nitrate was transported similar to chloride in free-flowing parts of the channel; however, nitrate was retained relative to chloride in a reach impacted by beaver dams (with Alan Jackman, University of California, Davis).

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TITLE: Solute Transport Involving Biological Processes in Surface Waters (WR 86-190)

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PROBLEM: Availability of toxic substances and nutrients to biota is dependent on their chemical form or speciation. Toxicological models, for example, have emphasized the effect of solute speciation on biological processes. Conversely, it has been demonstrated that partitioning of contaminants and nutrients can be affected by biological processes. Chemical processes that control chemical speciation in natural waters are solute complexation, precipitation and dissolution, sorption, and redox. Each of these processes affects and is affected by biological activity. Therefore, understanding and quantifying solute interactions with biota can be important in developing accurate water-quality models. Although inorganic and organic complexation have been emphasized in previous toxicological studies in chemically defined media, it is clear that chemical processes suppressed in these experiments can be important in natural water systems. The effects of biological processes on solute uptake and transport need to be quantified and incorporated in transport models.

OBJECTIVE: Study transport of trace inorganic solutes between particulates and primary producers. Examine and quantify processes controlling that transport (for example, adsorption onto and desorption from particles, and uptake and release from plankton and periphyton.) Establish how biological processes may contribute to the overall behavior of trace inorganic contaminants in surface-water systems.

APPROACH: Conduct field sampling and laboratory analyses to assess the chemical character of particulate and dissolved phases and to identify potentially important biological-transport processes. Determine trace-metal, macronutrient, and organic carbon and trace sulfide concentrations by means of various analytical and preparative techniques. Use chemically defined media, suspensions and algal cultures to describe processes controlling solute uptake and release by cells. Conduct laboratory culture experiments with field samples and isolates from natural planktonic and periphyton communities and generate biological transport models for testing and eventual incorporation into comprehensive water-quality models.

PROGRESS: A polarographic method, adapted from marine studies, was used for determination of trace sulfides in oxic waters (Detection limits of approximately 1 nM). Measurements made during the winter of 1990 and spring of 1991 in northern and southern San Francisco Bay indicated that sulfides exist at concentrations that may significantly affect metal speciation (and hence bioavailability) in the oxic water column. However, dissolved sulfides concentrations were typically not high enough to disregard competitive reactions between metals and dissolved organic matter. Longitudinal gradients observed in both components of the Bay for dissolved organic carbon were not observed for dissolved sulfides. Rather, a significant vertical gradient for sulfides suggested a primary benthic flux that will be quantified in upcoming experiments. An initial report on this study has been accepted for publication in the journal, Estuaries. A journal article on studies conducted at Whitewood Creek, South Dakota, contrasted processes responsible for diel changes in orthophosphate and dissolved arsenic species in a creek overlying an alluvial aquifer containing elevated solute concentrations. The interactive effects of phosphate and trace metals on phytoplankton biomass in Lake Tahoe, and the fragile chemical balance in this system that makes these interactions ecologically significant were described in another report. The journal article also provides the first dissolved trace metal data for the Lake water column. Work on the distribution and concentration of ATP and phytoplankton size and biomass is being prepared for journal publication.

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ECOLOGY

TITLE: Environmental Influences on Estuarine Benthic Community Dynamics (WR 86-192)

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PROBLEM: (1) Benthic invertebrate communities, composed of sessile, relatively long-lived species, provide a record of effects of short- and long-term environmental changes through species composition and abundance changes. Thus they are often used as water-quality indicators. However, their use in water-quality studies requires assumptions that communities remain at steady state except when influenced by human activity. Long-term studies show that natural variation over a variety of time scales often masks human-induced changes. (2) Estuarine benthic communities, often dominated by suspension feeders, have an unknown but potentially large controlling effect on phytoplankton biomass, and thus may be important in limiting eutrophication.

OBJECTIVE: (1) Characterize long-term patterns in estuarine and coastal benthic communities, in order to determine the contribution of natural factors (climatic events, seasonal/interannual patterns of runoff, water chemistry and circulation, sediment texture and stability, and food availability) to community variability, and to assess the contribution of human activity (waste contamination, control of river runoff) to the remaining unexplained variability in community dynamics. (2) Measure, through field and laboratory studies, the processes which determine the rates at which invertebrates remove phytoplankton from the water column.

APPROACH: (1) Quantitatively sample the benthos at regular intervals through time (and obtain access to data that have been collected by others) at fixed locations in various estuaries and nearshore habitats. Statistically analyze data from these samples for short- and long-term patterns of change in community structure and correlate these patterns through time-series analysis with both natural environmental factors and anthropogenic factors associated with the water column and sediment. (2) Determine the link between benthic community processes (feeding, respiration, substrate disturbance and stabilization) and changes in the water column (changes in planktonic biomass, nutrients, and organic matter) through field-manipulation experiments with transplanted animals and through laboratory experiments with individual species and intact infaunal communities in flumes that simulate changing field conditions.

PROGRESS: During Fiscal Year 1992, we continued studies of *Potamocorbula amurensis*, the clam recently introduced into San Francisco Bay, to document its spread and impact. A paper, nearing completion, characterizes the invasion pattern of this species in several different communities of the bay and examines how this pattern compares with invasions by introduced species in other systems.

Studies of the filtration rate of this clam have resulted in a new protocol for measuring filtration rate of infaunal invertebrates in laboratory flumes. A paper describing this protocol has just been published in the journal Marine Biology. Collaboration with researchers at Stanford University, who are looking at the hydrodynamics of filter feeding using models of the bivalves which we are using, has established the importance of certain hydrodynamic properties (bottom roughness and siphon height and orientation) in our flume studies. Work is presently underway to confirm the initial findings that filtration rate does indeed change with water velocity. To quantify possible ecological responses to organic contaminants in the benthic community (as part of the San Francisco Bay Toxic Substances Hydrology Program), we continue to characterize the long-term patterns of benthic community composition at seven fixed sites in northern San Francisco Bay to define the relationships between community structure and natural environmental perturbations, for example, responses to short- and long-term variations in river flow (changes in climate and subsequent alteration of salinity regime). A paper is being completed on the reproductive cycle of the dominant benthic organism (the Asian clam, *Potamocorbula*) throughout the bay, demonstrating that important differences in reproductive seasonality between north and south Bay may be related to a combination of food availability and osmotic stress. We are continuing the study of the growth of *Potamocorbula* in South Bay to determine how the spring phytoplankton bloom effects the growth cycle of the individual species. Initial results show the growth to be highest 3 months after the bloom. Therefore growth may be related to other organic matter or small phytoplankton blooms which are not seen in our sampling. A recently completed study of genetic variability in *Potamocorbula* at sites throughout the bay demonstrate that this species has high within-population genetic variability and limited genetic differentiation among sites. These features are indicative of a "general purpose" genetic strategy that provides this species with an inherent ability to invade and colonize new localities.

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GEOMORPHOLOGY AND SEDIMENT TRANSPORT

GEOMORPHOLOGY AND SEDIMENT TRANSPORT

TITLE: Movement and Storage of Sediment in River Systems (CR 75–102)

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PROBLEM: Sediment moves through a river system in response to specific events and changing conditions in the drainage basin. The movement of sediment is usually discontinuous. Episodes of movement are separated by periods of storage that can range from less than 1 year to more than 1,000 years. Understanding the movement and storage of sediment in rivers is important to navigation, flood control, and other aspects of river engineering, as well as to the prediction of the fate of contaminants absorbed on sediment particles.

OBJECTIVE: Assess (1) changes in river-sediment loads over periods of decades or longer and the factors (natural or artificial) that cause the changes; (2) rates at which sediment is stored in river systems and the residence times of sediment particles in storage; and (3) sources, pathways, and sinks of sediment particles in river systems.

APPROACH: (1) Assess long-term changes in sediment loads from data previously collected by U.S.Geological Survey and other agencies; (2) assess sediment storage by repeated (annual) surveys of selected river channels and by comparing old and new maps and aerial photographs of rivers and their flood plains; and (3) assess sources, pathways, and sinks by intensive field studies of selected large and small rivers.

PROGRESS: Two sampling cruises were completed on the Mississippi River between Minneapolis, Minnesota, and New Orleans, Louisiana. A resurvey of cross sections in Powder River, Montana, showed a moderate amount of channel change since last year. Meanders in Powder River are cut off mainly by upriver erosion of headcutting gullies across meander necks.

GEOMORPHOLOGY AND SEDIMENT TRANSPORT

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TITLE: Effects of Water and Sediment Discharges on Channel Morphology (CR 65-105)

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PROBLEM: Channels on alluvial streams change with time. Bed elevations and channel widths may change, meander bends shift both laterally and downstreamward, the sizes of the bed particles may change, instream bars grow and migrate, and the amount and type of vegetation along the river may increase or decrease. Sometimes the change is minor and insignificant, even over decades, but in other cases catastrophic modifications occur in minutes. The transformations can be natural or man-induced, and they can have significant effects on man and the environment.

OBJECTIVE: Determine and analyze the influence of the major governing variables, particularly water and sediment discharges, on channel morphology, and to evaluate how the many relevant variables and results change with time.

APPROACH: (1) Identify the major variables that govern channel morphology; (2) Obtain data sets that span as long a time period as possible; (3) Isolate the effects of different variables and analyze stream channels as dynamical systems, with an eye toward prediction of channel changes.

PROGRESS: Applicability of standard time-series analysis to chaotic systems was explored. Most studies in which data have been analyzed for possible chaos do not incorporate the usual tools of time-series analysis, probably because investigators are not aware of the applicability of such tools. Metric (Kolmogorov-Sinai) entropy is one of the critical indicators of chaos but unfortunately cannot be calculated for most data sets because data sets must be exceedingly large (on the order of tens of thousands or even millions of observations). Furthermore, it is an indicator that is poorly understood by many investigators. One of the most common procedures in chaos analyses is a calculation of Lyapunov exponents. However, even that tool suffers from the limitation that, with real-world data, only the non-negative exponents can presently be determined. All of the above-mentioned analyses are made difficult by the ever-present noise. I am exploring the possibility of applying chaos theory to channel morphology.

GEOMORPHOLOGY AND SEDIMENT TRANSPORT

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TITLE: Hydraulics and Mechanics of Bedload-Transport Processes (CR 74-187)

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PROBLEM: Of all processes operating in river channels, and especially of those of practical concern to engineers and others interested in river-channel behavior, perhaps the least information is available regarding the hydraulics and mechanics of bedload transport. As scientific knowledge of river behavior advances and is applied to management of the nation's rivers, additional understanding of bedload-transport processes will be necessary.

OBJECTIVE: (1) Define (a) spatial and temporal variations in transport rate and particle size of bedload; and (b) the average magnitudes of transport rate and particle size throughout a range of geographic locations, channel geometries, and river hydraulics. (2) Evaluate the adequacy of sampling equipment and field procedures, provide interpretation of bedload-transport processes, and assess the applicability of existing or new predictive techniques in river hydrology. (3) Demonstrate the value of sediment data in designing hydrologic networks and in evaluating regional and temporal trends in water-resources information. (4) Assess the usefulness of numerical simulations as hydrologic tools in fluvial geomorphology. (5) Provide interdiscipline perspectives in evaluation of environmental resources (for example, fishery habitat), impact assessments (for example, alluvial mining), and management alternatives (for example, operating policy). (6) Apply the information to operational programs of the USGS and other organizational units to assist in the solution of practical problems.

APPROACH: (1) Use continuous sampling of bedload (for example, conveyor-belt bedload trap on the East Fork River near Pinedale, Wyoming) as a control to evaluate spatial and temporal variability factors in bedload transport and to evaluate general relations between sediment movement and river hydraulics. (2) Field calibrate the sediment-sampling efficiency of the Helley-Smith bedload sampler simultaneously with operation of the bedload trap. (3) Use the calibrated Helley-Smith sampler and the concurrent measurements of streamflow hydraulics in the systematic collection of bedload samples from a variety of sand- and gravel-bed streams, and within the laws of general physics, stochastically develop empirical relations of bedload transport and interpret the physical significance of the developed relations. (4) At the conveyor-belt bedload-trap research facility, initiate a tracer study using fluorescent particles (sand to fine gravel) to evaluate (a) residence time of sediment (b) average speed of various sizes of particles

(c) depth of bed material involved in transport (d) dispersion of bed material (e) short-term channel changes accompanying sediment transport (f) influence of availability of sediment on transport rate and (g) other related aspects of sediment transport. (5) Extend the fluorescent-tracer study to larger particles (coarse gravel to cobbles) by implanting microradio transmitters in individual rocks and, by periodic and (or) continuous detection by receivers/data loggers, provide time-sequence data on motion and location of separately identifiable particles. (6) Establish field sites for bedload sampling that document varying characteristics of geographic coverage (factors of hydrology, meteorology, soils, biology, and so forth); maintain one or more bedload stations as long-term observation sites so that time-trend data can be evaluated. (7) Initiate and participate, as needed, in studies comparing sampler types, sampling procedures, and analytical techniques to formulate and modify guidelines on equipment needs and field/laboratory practices; provide emphasis on relevancy to WRD mission and on need for consistency of data collection. (8) In conjunction with biologists, chemists, and other scientists, develop a field-oriented strategy for comprehensive environmental assessments; apply developed strategy to specific sites to demonstrate and document sediment-related variables as important ecological factors.

PROGRESS: (1) Field work at the bedload trap and for the fluorescent-tracer study is complete. Bedload-transport rates measured synoptically, vary along a river reach; bedload tonnage, measured seasonally, is about constant throughout the reach. Mean bedload-transport rates relate to streampower (about the 1.6 power of streampower in excess of streampower at initiation of motion), mean bedload-particle speeds are slow (about 0.1 percent of water speed), and lengths of particle movement may be seasonally limited. (2) Radio transmitters were implanted in cobble-size rocks and movements tracked as part of studies on Toklat River, Lignite Creek, and Phelan Creek, Alaska. Bedload-transport rates relate about to the 1.6 power of discharge in excess of discharge at initiation of motion and particle size (mean, modal, and maximum) increased as transport rate increased. Motion sensors allow distinction between periods of motion and periods of inactivity. Generally, brief periods of motion are followed by longer times of rest. Large moving particles (about fist size) travelled about the same distance as smaller particles (about golf-ball size). Particle speeds and distances travelled are in general agreement with observations from East Fork River, Wyoming. (3) Long-term data collection continued for the 10th year at Little Granite Creek, Wyoming (in cooperation with the Idaho District, USGS). Although measured total-sediment loads are among the longest data sets available at a continuous-record gage, the period of record is still short to forecast time trends. Generally, during the period of observation, water runoff has decreased and sediment yields have lessened more dramatically. These facts may be related to short-term weather variability rather than to long-term climate change. (4) Comparisons of equipment and procedures were continued in collaboration with personnel in other countries and from other USGS offices. This was highlighted by a month-long visit to the Peoples Republic of China (PRC), under the USA-PRC Protocol, to evaluate bedload equipment and sampling techniques. (5) In collaboration with other

USGS scientists and academia personnel, environmental assessments were conducted on several streams in Yellowstone and Denali National Parks, Wyoming and Alaska. A field procedure to evaluate habitat quality was developed combining geomorphic aspects (river hydraulics, sediment characteristics, topography), water chemistry (pH, conductance, trace elements, organic carbon), and biological factors (benthic drift, invertebrates, fish). (6) Studies of phytoplankton taste and odor problems were established on Fremont Lake; interpretations are complete and a report is in press.

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TITLE: River Mechanics (CR 82-273)

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PROBLEM: The geometry and pattern of river channels adjust to significant changes in the water discharge, size, and quantity of sediment supplied to the channel. When the quantity of water and sediment over a period of years remains relatively constant, the channel geometry and pattern vary about a mean or quasi-equilibrium condition. Major watershed alterations that change the supply of water, sediment, and size of sediment reaching the channel necessitate an adjustment of the channel geometry and pattern. That is, the channel is transformed from one quasi-equilibrium state to another. Between the two quasi-equilibrium states, there is a period of instability and adjustment. Existing techniques for examining and predicting river channel adjustment have been developed primarily from investigation of quasi-equilibrium rivers. As a result, it is frequently possible to predict with a modest range of uncertainty the future quasi-equilibrium hydraulic characteristics of a river following a change in its watershed. The dynamics and rate of river channel adjustment during the period of instability, however, have rarely been studied, and are rather poorly understood. The length of time required for the complete adjustment is commonly a few decades to a century or more. In many instances, such as surface mines, reservoirs, and urbanization, the adjustment period may, in fact, be longer than the duration of the watershed change. In watersheds where various land-use changes occur every several years, river channels may be continually adjusting to different contributions of water and sediment, and thus, never reach a quasi-equilibrium condition. In these rivers, instability and adjustment are the prevailing condition. The primary focus of this research project is to understand the dynamics and rate of river channel change and develop numerical models to make predictions of river channel characteristics given a particular change in flow regime and sediment supply. The greatest deficiencies in our present knowledge of river channel adjustment are (1) the longitudinal sorting of bed material, especially gravel, (2) the formation and stability of bed forms, (3) adjustment of channel width through the erosion and deposition of bank material, and (4) the rates at which the several hydraulic variables adjust.

OBJECTIVE: Develop physically-based numerical models to describe the processes and rate at which a river channel adjusts in response to a change in the water discharge, sediment size and sediment load supplied to the channel. Emphasize the adjustment of those aspects of river channels known to significantly influence the aquatic ecosystem, that is, the bed-material size distribution, occurrence of bars, and channel width. Describe the hydraulic processes controlling these characteristics of river channels as well as the rate at which they function. Formulate mathematical models of the processes as required for longitudinal routing of water and sediment. Develop new analytical tools for describing river-channel adjustment.

APPROACH: The development of physically-based hydrodynamics models involves an iterative process of model formulation, testing model predictions using field and laboratory measurements, and then model refinement. Precise field and laboratory measurements are essential. Ideally, one would study in great detail the transition of a river channel from one quasi-equilibrium state through a period of instability to another quasi-equilibrium state as a result of a known change in the supply of water and sediment. Unfortunately, this approach is impractical for several reasons including the need to maintain a high level of effort over the period of adjustment, which may last for a few decades to a century or more. Instead, one must limit the detailed study of processes to a duration much less than would normally be required for channel adjustment. These studies, however, can lead to a precise description of physical processes. Although historical information is incomplete and less precise, the course and rate of river channel adjustment through time can only be understood by studying historical examples. Thus, reconstructions of the sequence and rate of channel adjustment using historical examples of river channel change are necessary components of this research. Better understanding of river channel adjustment requires a combination of precise field and laboratory studies, the reconstruction of historical examples using available information, and carefully formulated physically-based models.

PROGRESS: During the 1991 fiscal year, significant progress has been made on several topics of on-going research: (1) the nature of flow over bed forms, (2) incipient particle motion and marginal sediment transport of coarse material in natural streams, and (3) the nature of circulation and sediment accumulation in lateral separation eddies. A cooperative effort with the University of California at Santa Barbara concerning the nature of flow and turbulence structure over two-dimensional bed forms was initiated in 1989. A series of laboratory flume studies was begun in August 1990. Analysis of a portion of the laboratory measurements has been completed, which provides a much improved description of turbulent stresses over bed forms. These results, also, lead to a very precise method for calculating the flow velocity profile and the equilibrium amplitude of bed forms. A manuscript has been submitted for publication. A model for marginal bed load transport was derived where the transport rate is given by the product of the particle mass, the number of particles in motion per unit area, and other particle velocity. Both the number of particles in motion and the particle velocity are specified functions of the dimensionless shear stress and particle size. The effects of boundary roughness, particle shape, particle orientation, and packing of bed particles are also specified, in order to determine the number and velocity of bed particles in motion. Predicted bed load transport rates using the model are in good agreement with laboratory flume measurements for three sizes of uniformly sized bed material, 2.5 mm, 7.95 mm, and 22.2 mm, described by Paintal (1971). The study of lateral separation eddies consists of a combination of field, laboratory, and theoretical work aimed at understanding the mechanics of flow and sediment transport in eddies. One flume experiment has been completed, and several locations have been studied and analyzed for their suitability as a comprehensive field study. A numerical model has been developed for computing the deposition rate of sand throughout a lateral separation eddy. The model solves the advection-diffusion equation for a mixture of suspended sand-sized sediment. These computations demonstrate that eddies are typically very effective sediment traps, because the Rouse number of an eddy is commonly one-fifth to one-tenth of the value in the primary channel and the residence time of water in the eddy is large compared to the ratio of the flow depth to the particle settling velocity. Typically, deposition rate for a river such as the Colorado River is several centimeters per day at discharges near the mean annual peak.

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TITLE: Sediment-Transported Pollutants in the Mississippi River (CR 87-309)

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PROBLEM: The source and fate of many pollutant substances in the Nation's largest river system are closely tied to suspended sediment. Accurate prediction of the fate of these pollutants will require more than our present understanding of the interactions between sediments and pollutants and the ways in which large rivers store and remobilize suspended sediment.

OBJECTIVE: Define and understand (1) processes by which pollutant substances, organic and inorganic, are adsorbed onto sediment particles; (2) downstream mixing of pollutants below the confluence of large tributaries with the mainstem; and (3) seasonal storage and remobilization of sediment and pollutants in the Mississippi River system.

APPROACH: One to two boat trips per year, beginning at Minneapolis, Minnesota, and ending at New Orleans, Louisiana, will be made to sample 15-20 cross sections of the Mississippi River and its principal tributaries. Cross sections will be sampled with a large-volume suspended-sediment sampler by the equal-width-increment method. Suspended sediment will be concentrated and analyzed for a large number of organic and inorganic constituents, both natural and manmade. New methods for sampling and analyzing pollutants attached to sediment particles will be developed in the field and in the laboratory.

PROGRESS: Two full-scale chemical sampling trips were made on the Mississippi River between Minneapolis and New Orleans during September–November 1991 and March–May 1992, bringing to 10 the final number of such cruises made during 1987–92. Representative composite bed-material samples were collected from 25 of the navigation pools of the upper Mississippi. The herbicide atrazine was present in all samples collected from the Mississippi River and its tributaries, and it reached concentrations in excess of MCL in several tributaries during the herbicide-application season. Industrial organic compounds are adsorbed onto suspended-sediment and bottom-sediment particles in the river: the distributions of some, like hexachlorobenzene, reflect source areas in the Ohio River and in the Lower Mississippi River below Baton Rouge; the distributions of others, like PCBS, show how sediment in the river can be homogenized by successive years of deposition and resuspension.

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TITLE: Sediment Impacts from Disturbed and Undisturbed Lands (CR 79-311)

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PROBLEM: The acquisition and meaningful interpretation of sediment data from areas disturbed by land-use activities or natural processes is one of most deficient areas of recognizing nonpoint-source pollution in the United States. The comparison of sediment data from disturbed and undisturbed areas provides a means to (1) evaluate the effects that land-use activities cause, (2) investigate the geomorphic processes that regulate the detachment and transport of sediment, and (3) develop strategies for remedial action to reduce excessive sediment discharges. This information is especially necessary to minimize sediment discharges and sorbed chemical loads from surface-mine, industrial, agricultural, and urban areas.

OBJECTIVE: (1) Evaluate the extent and utility of sediment data from a variety of land-use areas; (2) predict the movement of sediment from drainage basins affected by those land uses; and (3) assess existing techniques and develop new ones based on geomorphic principles and the application of statistics, geochemistry, and botany to the limited data available as aids in improving our interpretive capabilities.

APPROACH: Field investigations are being conducted to evaluate available techniques for predicting sediment yields. Of particular interest are the Water Erosion Prediction Project model and the U.S. Department of Agriculture (USDA) rainfall simulation model. Research is to be conducted to develop technology for determining (1) pre-disturbance sediment-delivery ratios (proportion of gross erosion that appears as sediment yield at some place in the watershed) based on factors such as land use, contributing drainage area, runoff, basin morphology, relief, vegetation, and geochemical tracers, (2) sediment yields during disturbance, which are influenced by sediment-control measures used during land-use activity, and (3) sediment-delivery ratios for the post-disturbance period. In cooperation with other agencies and field offices of the Survey, available sediment and related hydrologic and chemical data are being acquired and interpreted to develop techniques and possibly models to aid in the prediction of sediment impacts from land disturbance.

GEOMORPHOLOGY AND SEDIMENT TRANSPORT

PROGRESS: The USDA rainfall-simulation model was combined with geomorphic field techniques to yield estimates of total annual runoff and ground-water recharge in watersheds of the United Arab Emirates and the Amargosa River basin (as part of the Nuclear Hydrology Program). These methods are first steps towards developing quantitative water-budget estimates and eventually sediment discharges from undisturbed watersheds of arid and semiarid areas. A second USDA model, the chemicals, runoff, and erosion from Agricultural Management Systems model, was also used to develop a technique to estimate upland or cultural groundwater recharge during infrequent events of heavy precipitation. The combined results of the two techniques provide estimates of total mean annual recharge.

For many watersheds a large portion of total sediment discharge occurs in less than 1 percent of time. Sediment discharge, geomorphic changes and vegetation changes are being studied in the Plum Creek basin, Colorado, following an historic flood in 1965. Substantial progress has been made in understanding the distribution of flood deposits in study reaches, relating the 1965 event to the paleoflood record, defining total-load sediment discharges in the basin, and understanding the reestablishment of willow and cottonwood trees along Plum Creek.

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TITLE: Sediment-Water Chemistry in Large River Systems: Biogeochemical, Geomorphic, and Human Controls (CR 88-313)

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PROBLEM: Rivers are a major pathway to the ocean for erosion products and human wastes. The mechanisms that control the composition of river-borne materials are only imperfectly understood because erosion and the subsequent transport of material by rivers are mediated by a wide variety of closely linked chemical, biological, and physical processes. Moreover, in developed river systems such as those in the United States, these processes are subject to pervasive human-related perturbations. There is a need to develop, through field and theoretical studies, a comprehensive and integrated description of these processes for large river systems in a form that is useful to researchers in many disciplines.

OBJECTIVE: Describe how the biogeochemical and physical aspects of erosion and transport processes are reflected in the composition of river-borne materials for particular large river systems and develop general theoretical models that can be applied to rivers in general; evaluate the extent to which human activity has affected the river systems. Study how various chemical phases, natural or human-introduced, organic or inorganic, are partitioned between solid and dissolved loads in rivers and estuaries as the result of weathering, particle-surface reactions, biological uptake or release, atmospheric exchange, and storage during transit. Evaluate the dispersal pathways of river-borne substances through river systems and estuaries into and across the coastal marine environment.

APPROACH: Assemble, primarily from maps and data bases, current and historic chemical, geomorphic, biological, and demographic data for an entire river system. Identify phenomena that are especially important in controlling the composition of phases containing the major elements (H, C, O, Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Fe) and certain minor indicator elements (N, F, P, Mn, Sr, Zr) to provide the conceptual framework for solving specific research objectives. Undertake field surveys, design sampling and analytical procedures, and create computer tools to manipulate and model data as part of these investigations. Formulate small scale field and laboratory studies to aid data interpretation as deemed necessary.

PROGRESS: In Fiscal Year (FY) 1992, project efforts concentrated on investigations of weathering and erosion processes, nutrient cycles, and gas exchange in small tropical watersheds. This research is related to the USGS Global Change Program. Sites are in northeastern Puerto Rico, at the Luquillo Experimental Forest (LEF), and in central Panama, at the Barro Colorado Nature Monument (BCNM). Work at the LEF is funded under the Water, Energy, and Biogeochemical Budgets (WEBB) Program of the USGS-WRD. The Smithsonian Tropical Research Institute shares funding for the work in Panama. These studies are designed to compare geologically matched natural and developed environments. The studies of weathering and erosion use long-term chemical sampling and physical monitoring to characterize the processes that control the distribution and transport of major, important-minor, and nutrient elements through soils, downslope, and out of the watershed. Phenomena of interest to global-change research include the fixation, storage, and export of carbon and nutrients as related to biogeochemical and geomorphic processes within the watersheds. During FY 1992, the sampling and analysis of samples from selected rivers began in both Puerto Rico and Panama. In addition, regular samples of precipitation, soil water, and surficial runoff are being collected and analyzed. Collection apparatus and monitoring equipment have been installed for event sampling in most of these streams, and preliminary event sampling has begun. By the end of the fiscal year, elemental analysis of all sediment, soil, and bedrock samples collected from these watersheds will be completed. In addition to this work in Puerto Rico, exploratory work is to be done on collecting a smaller but similar series of samples from South Cascade Glacier in Washington. The glacial basin has high runoff and bedrock similar to that in the study watersheds of Puerto Rico. There is, however, virtually no vegetation, thus it may be possible to distinguish purely chemical weathering processes from those that are biologically influenced.

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GEOMORPHOLOGY AND SEDIMENT TRANSPORT

TITLE: Applications of Fluid and Sediment Mechanics to Basin and Regional Scale Hydrologic and Geomorphic Problems (CR 91-324)

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PROBLEM: Stream systems function as integrated units from the zero-order basins at their heads to their terminations at the sea. Interior adjustments to changes in their headwaters or along their lengths occur in a variety of ways, some of which leave sedimentary deposits that provide important information with regard to the sensitivity of the systems to disturbances of various magnitudes and with respect to the nature of past disturbances. The former type of information is crucial to reliable interpretation of paleoflood deposits and the latter knowledge is essential for testing hydrologic predictions derived from climate models. In order to interpret fluvial deposits properly, however, an extremely accurate knowledge of stream system mechanics is required.

OBJECTIVE: The long-term goal of this project is to develop precise, process-based algorithms for flow, sediment transport, stream channel adjustment, erosion, and deposition in characteristic segments of a wide variety of fluvial systems. These algorithms then can be used to assess local environmental problems along particular types of stream segments, or they can be coupled with each other and with analogous algorithms for hill slope processes in order to produce models for erosion, sediment transport, and deposition on a regional scale and, thereby, provide a sound, process-based connection between regional hydrology and the salient characteristics of the sedimentary deposits in a wide variety of stream systems.

APPROACH: Stream systems are far too complex to be understood using empirical data only, but mathematical models that are to be used to provide reliable information from extreme or past events must be predictive in character and they must be devoid of parameters that make calibration of the models necessary. These models must be thoroughly tested using data from comprehensive studies of carefully chosen natural systems. The complex morphology of river channels and the intricate topography of hill slopes is generally not well known, and, thus, cannot be treated effectively in a completely deterministic fashion. In contrast, the flow and sediment transport over these surfaces usually can be computed with reasonable accuracy from available fluid mechanical theory if the topography is known. Comprehensive, processes-based flow and sediment transport models for rivers and hill slopes, therefore, must represent the topographic elements in an appropriate stochastic manner while treating the response of the flow to this topography in a proper deterministic fashion. Models that are useful for environmental reconstruction require the judicious combination of modern fluid mechanical theory with a carefully crafted statistical treatment of the surface over which fluid is moving, so that the dominant nonlinear interactions between the topography and the flow are fully characterized and the evolution of the landscape is accurately represented.

PROGRESS: Because of the sensitivity of fluvial processes in arid regions to variations in climatic parameters, the importance of water for irrigation and hydroelectric power in the arid West , and the need for models that clearly and conclusively show the environmental effects that do and do not occur from engineering works and natural causes, the Colorado River was chosen as the first system to be examined in detail. As a consequence of uplift of the Colorado Plateau in the late Tertiary, many segments of this system are deeply cut into bedrock, and there is substantial present interest on the part of various bureaus of the Department of Interior in improving the current understanding of processes in the incised reaches of this system. Of particular note in this regard are the U.S. Geological Survey-Bureau of Reclamation project in the Black Canyon of the Gunnison and the extremely important, multi-agency project in the Marble and Grand Canyons (called GCES-II). Reliable models for the fluvially driven processes in such systems are lacking.

Funding from the U.S. Bureau of Reclamation for U.S. Geological Survey research on the Colorado River between Lake Powell and Lake Mead has made possible a major thrust toward understanding flow, sediment transport, erosion, channel adjustment, and deposition not only in this important segment of the Colorado River, but also in deeply incised systems in general. The Arizona District Office of Water Resources Division, and several National Research Programs and Geological Division Projects, are contributing in a major way to this research effort. The primary role of the project Flow and Sediment Mechanics has been, and continues to be, fluid mechanically based analysis of the main channel flow and sediment transport data and the development of flow, sediment transport, channel adjustment, erosion, and deposition algorithms. These efforts are tightly coupled to comprehensive field data collection programs being superbly carried out by personnel from the Arizona District. Work to date on these topics is summarized in a manuscript entitled "Flow and Sediment Transport in the Colorado River Between Lake Powell and Lake Mead" by J. Dungan Smith and Stephen Wiele. This manuscript is currently undergoing internal review. A local investigation of flow and sediment transport in the neighborhood of the National Canyon gage site also is underway. In this study, velocity and suspended sediment fields measured at the cable by Arizona District personnel are being used to test the predictions of process-based, quasi three-dimensional models derived specifically for this site. Once verified, the suspended sand transport model will be used to produce a sediment rating curve for this site, and this sediment rating curve will be used to provide a boundary condition for the less sophisticated whole segment sediment transport model. This work will be presented in a manuscript by Schmeeckle, Christiansen, and Smith during the coming year.

Flow in the Colorado River originally was controlled by snow melt in its head-waters; whereas, the sediment input always has been of a more local origin. Currently the major sources of sediment to the Marble and Grand Canyon reaches of the Colorado are the Paria and the Little Colorado Rivers. In both cases, the dominant contribution of material is as suspended load, and in order to provide a more accurate means of determining the amount of sand added to the Colorado below the Glen Canyon Dam, process-based methods for calculating suspended sediment input from these major tributaries are being developed. These models ultimately will be tested against data from the major sand transporting tributaries of the Colorado River and then will be used to calculate sediment inputs from the ungaged tributaries, as well as variations in sediment input with land use and climate from the gaged ones. This work will appear in a manuscript by Topping and Smith.

Another investigation relevant to the Marble and Grand Canyon reaches of the Colorado River involves the mechanics of erosion of bedrock and of particle size reduction by pulverization at the downstream sides of debris fans. Also, it is believed by the project chief that this is the dominant mechanism through which rapid incision occurs in the steep head-waters of tectonically active systems. Finally, work is continuing on the mechanics of debris flows. This research by Schmeeckle and Smith was initiated at the University of Washington, under funding from the Office of Naval Research, in order to understand slumping on silty faces of large deltas, but it also is directly relevant to the development and structure of debris fans in the Grand Canyon and to the rapid movement of lahars down valleys on the flanks of active volcanoes.

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TITLE: Response of Fluvial Systems to Climatic Variability (WR 89-200)

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PROBLEM: Understanding the effects of climatic variability is important to development of water resources, mitigation of flood hazards, and interpretation of geomorphic surfaces. Climatic variability, which is characterized by temporal changes in variability of seasonal climate that spans decades or centuries, may be more important to water-resources evaluations than changes in mean climatic conditions. Changes in variability of climate has a large effect on the probability of occurrence of extreme events, such as floods or droughts. Understanding of climatic variability and its effect on the landscape is of paramount importance for estimation of flood frequency, sediment transport rates, and long-term watershed and channel changes.

OBJECTIVE: The objective of this project is to define historic climatic variability in the western United States over the past century; to identify specific time periods of statistically stationary precipitation, discharge, flood frequency, and sediment transport; and to assess the net effects of climatic variability on watershed conditions and fluvial systems.

APPROACH: Historic climatic variability will be assessed through regionalization of temporal climatic signals including temperature and precipitation amounts and intensity. Proxy synthetic records such as tree-ring widths, varved ocean sediments, and non-anthropogenic changes in vegetation will be determined. General circulation of the atmosphere will be examined for long-term changes in precipitation-generating mechanisms that affect the western United States. Generation mechanisms for specific storm types, which include tropical cyclones and winter frontal storms, will be examined for frequency changes in time and space. Paleoflood records will be developed for rivers that are sensitive to climatic variability. Regional flood frequency, streamflow, and precipitation models will be used to assess the effects of variability changes. The stability of desert vegetation will be assessed to determine possible interactions among climate, vegetation change, and storm runoff.

GEOMORPHOLOGY AND SEDIMENT TRANSPORT

PROGRESS: Research under this project has been focused on development of new dating techniques and reconstruction of environmental changes over the past century on the Colorado Plateau. Dating of alluvial sediments using ^{137}Cs appears promising and potentially as accurate as post-bomb ^{14}C dating. Dendrochronological analyses of catclaw trees (*Acacia greggii*), a common tree in Grand Canyon, yielded cross-dating between this species and conifers. If tree-ring dating of catclaw proves feasible, this species has a large potential for dating ungaged floods and reconstructing the occurrence of floods in isolated areas of the Sonoran Desert. In Grand Canyon, repeat photography has demonstrated a century-long persistence of about 40 species of desert plants, most of which previously were of unknown longevity. Increases in certain species in the photographs indicates that a decrease in frost frequency, which likely occurred around the turn of the century, has affected the Grand Canyon and probably much of the southwestern United States. In addition, the frequency of debris flows in Cataract and Grand Canyons, reconstructed using a combination of alluvial stratigraphy, repeat photography, and dendrochronology, was found to be higher than previously expected. The results, in concert, represent one of the first interdisciplinary efforts at reconstruction of environmental change over a century in an isolated place.

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GROUND-WATER CHEMISTRY

TITLE: Transuranium Research (CR 77-223)

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PROBLEM: Information is very limited on the speciation (oxidation-state distribution, solubility, hydrolysis, and complex formation) of plutonium and other transuranium elements in ground waters. These speciation data are vital to the accurate prediction of long-term mobilization and transport of these long-lived radionuclides from nuclear-waste repositories.

OBJECTIVE: Define the chemical speciation (and hence mobility) of transuranium elements (primarily plutonium) as a function of ground-water composition, pH, and redox potential.

APPROACH: Obtain ground-water samples of interest from the Idaho National Engineering Laboratory (INEL) and possibly other sites. (Other sites have not been selected, but one possible site under consideration is the Underground Research Laboratory at the Whiteshell Nuclear Research Establishment, Pinawa, Manitoba). Techniques involve addition of known quantities of plutonium, pre-adjusted to the reduced [Pu(III) and (IV)] or oxidized [PuV) and (VI)] forms to measured volumes of each of these waters, place in tightly sealed Teflon vessels, and allow to stand in darkness for periods of 17 and 30 days. At the conclusion of the specified time period, mix well, sample, filter through a 0.1-micrometer filter and sample again. The plutonium in the filtrate is defined as being soluble. Determine the oxidation-state distribution of the soluble plutonium by carrier precipitation and solvent extraction techniques. Repeat the solubility determinations using americium(III). Run five replicates for each set of parameters. Attempt to correlate plutonium solubility and oxidation-state distribution and americium solubility to the chemical composition and redox properties of the ground water.

PROGRESS: Studies have concentrated on ground waters from the Radioactive Waste Management Complex (RWMC) at the Idaho National Engineering Laboratory (INEL). Speciation and solubility studies on plutonium and americium were conducted on seven ground waters from RWMC, specifically the production well and wells 87, 88, 89, 90, 92, 117, 119, and 120. In the high-oxidation-state runs, plutonium was soluble in all the waters, whereas varying results were obtained in the low-oxidation-state runs. Plutonium was most soluble in Well 92 water (90 percent after 30 days (percentage relates to the amount of plutonium originally added)); it was least soluble (5 percent) in Well 89 water. Plutonium solubilities in the other waters ranged from 20 to 50 percent, and in 5 of the waters studied Pu(IV) was the predominant oxidation state, an unexpected finding. Because the chemical compositions of the waters were similar and unremarkable, it was concluded that the variations in plutonium solubility were caused by differences in the redox properties of the waters. Americium solubilities were relatively low (less than 40 percent) in all waters, and lowest of all in well 88 (9 percent). We concluded that although solubilities in some cases are limited, they are always high enough to cause a significant migration potential.

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TITLE: Geochemistry of Clay-Water Reactions (CR 82-276)

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PROBLEM: Clay minerals can influence the chemistry of ground water and other aqueous solutions through precipitation, dissolution, and ion-exchange reactions. An understanding of these reactions is crucial for predicting the behavior of toxic wastes in disposal areas. How do the various clays react with waters of varying composition at different temperatures and pressures? After the fundamentals of these processes are understood, how can they be applied to prediction, maintence, and (or) improvement of water quality?

OBJECTIVE: (1) Develop a theory for ion exchange that would allow prediction of the exchange properties of a clay on the basis of clay's crystal chemistry; (2) gather basic information on clay-mineral structure and chemistry; and (3) try to understand the precipitation and alteration of clay minerals in natural and synthetic systems.

APPROACH: Test and develop theoretical models through laboratory experiments (for example, measurement of exchange isotherms with well-characterized clay minerals). Study clay-water reactions in natural systems in the field.

PROGRESS: We continue to work on slow-release, nonpolluting fertilizers. A patent has been applied for a slow-release N-fertilizer. We manufactured a ton of this fertilizer for experimentation during the 1991 and 1992 growing seasons at the Management Systems Evaluation Areas (MSEA) sites in Missouri, Iowa and Nebraska. We also discovered and are patenting a slow- release P-fertilizer that uses low-grade P rock that should give excellent results in tropical soils. This fertilizer can be used in conjunction with the slow-release N-fertilizer for which the patent application has already been filed.

Our project has discovered that many minerals in sedimentary and metamorphic environments react by Ostwald ripening and thus contain a detailed record of their recrystallization history. We are extending our knowledge of the ripening process by: (1) trying to derive a common rate law for such recrystallization; (2) running hydrothermal experiments (with Whitney, Geologic

Division) to measure rate constants and activation energies for illite recrystallization; (3) developing methods for measuring particle size distributions for clays, including use of the Atomic Force Microscope (with Alex Blum) and The Warren-Averback X-ray Technique; and (4) studying the structure, chemistry, and isotopes of clays as a function of particle size (with Polish geologist Jan Srodon). We also are beginning to synthesize specific absorbers that could be used in pollution control and will be used to test Eisenman's model for ion exchange.

Our project (May) is completing development of a high-precision dissolution calorimeter for determining or improving as yet unknown or imprecise thermodynamic properties of clays, zeolites and other aquifer minerals. May also is developing and testing computerized, mobile water analysis laboratory vehicles for a USGS group and for the National Radioactive Waste Agency of Spain.

Not included in the following bibliography are the following papers that are either in review or in press: "Low temperature dissolution of clinochlore at pH 3, 4, and 5 (Acker, Bricker and May); "Co(II) sorption on kaolinite, Parts I and II" (O'Day, Parks, and May); "Three zones for illite formation during burial diagenesis and metamorphism" (Ebert); Zeolite (NH_4-clinoptilolite) influence on elemental concentrations in sorghum-sudangrass (Eberl, Barbarick, and Lai); and "Zeo-agriculture (Eberl).

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TITLE: Environmental Dynamics of Persistent Organic Compounds (CR 83-283)

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PROBLEM: Many persistent organic compounds are hazardous to human and ecological health. The transport characteristics of the compounds across environmental interfaces are strongly influenced by adsorption and partition interactions with the individual phases. Quantification of process rates and partition constants of organic pollutants in air, water, soil, and biota is an important step in defining the level of organic contaminants in environmental systems and their potential effects on environmental quality.

OBJECTIVE: Delineate and quantify processes affecting the movement and distribution of persistent organic compounds in hydrogeologic systems. (1) Determine the sorptive capacity of soil and sediment from air and water; (2) identify the roles of soil and sediment organic matter, mineral components, and moisture in sorption of organic compounds; (3) establish the physical basis of bioconcentration and lipophilicity of organic compounds; and (4) characterize the effect of dissolved organic matter on the solubility and mobility of organic contaminants in natural water.

APPROACH: Make laboratory measurements to determine the sorption of various organic compounds from water, analyzing data in terms of the properties of the compounds and soil constituents. Study sorption from the vapor phase to determine the effect of soil moisture. Make measurements to determine the alteration of the apparent water solubility of solutes by dissolved organic matter from various sources. Measure the partition coefficients of solutes in solvent and lipid-water systems to obtain information related to bioconcentration. Collaborate with field researchers to relate laboratory findings with field data obtained from organic-contamination sites.

PROGRESS: The suitability of chemical agents to be used in surface area measurement of soil organic matter (SOM) and minerals were investigated. The markedly higher "surface area" of SOM (560–800 m^2/g) based on retention of polar liquids (such as ethylene glycol) over the corresponding BET-(N_2) surface area (about 1 m^2/g) is ascribed to the high solubility of polar liquids in SOM, making the former method grossly unreliable for surface area determination of SOM and (or) natural samples containing large amounts of organic matter. The assumption by others that SOM possesses large internal surfaces as measured by the SOM's uptake of polar liquids cannot be justified on the basis that these surfaces are not accessible to low-molecular-weight inert gases, such as N_2. In other studies, we investigated the effect of SOM composition and water saturation in SOM on the partition of organic compounds from aqueous and vapor phases. In aqueous systems, where the organic solute uptake by soil is effected mainly by solute partition in SOM, the observed solute partition coefficient between SOM and water (Kom) increases with a decrease of polar group content in SOM. For given solutes in "normal soils," the Kom values vary by less than a factor of 3. The partition effect of organic compounds in dry SOM is found to be a factor of 2 higher than that in water-saturated SOM. The observed reduction by water saturation of chemical partition (solubility) in SOM is only moderate in comparison with the corresponding suppression by water saturation of the adsorption of organic compounds on soil minerals. The results suggest that the major effect of water in a drying-wetting cycle on organic compound uptake by low-organic-content soils (and the associated compound's activity) is the suppression of adsorption on minerals rather than the mitigation of the partition in SOM.

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GROUND-WATER CHEMISTRY

TITLE: Reaction-Transport Modeling in Ground-Water systems (CR 89–318)

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PROBLEM: In order to address urgent problems in contaminant migration and to understand many natural geologic processes, we need to be able to model the movement of substances undergoing chemical reactions in ground-water systems. Predictive models will be used to assess the risks of nuclear- and chemical-waste disposal, to analyze contaminant migration from pollution sources, and to determine the susceptibility of aquifers to contamination. Models also are needed to investigate many rock-water interactions, such as the formation of ore deposits and the evolution of ground-water chemistry.

OBJECTIVE: The long-range goals of the project are (1) to develop reaction-transport models with varying levels of complexity and data requirements, providing guidelines for the appropriate application of these models given field conditions and limited resources; (2) to incorporate the effects of surface-chemistry phenomena into reaction-transport modeling; (3) to develop methods to identify and quantify important chemical and biological reactions affecting transport of inorganic and organic substances; and (4) to compile estimates of reaction rates and reaction-rate laws for chemical and biological reactions.

APPROACH: The fundamental approach of the project is to develop computer models describing the movement of chemical substances in reacting systems that can be applied to field and experimental data. The project will begin by enhancing and streamlining geochemical-reaction models to make them suitable for inclusion in reaction-transport codes while studying the available literature on solute transport and reaction modeling. Two models will then be developed to test the pure differential equation approach and the coupled reaction and transport approach.

PROGRESS: A Water-Supply Paper for the Central Oklahoma National Water-Quality Assessment (NAWQA) project was submitted for Director's approval. The paper describes one of the first times a ground-water flow model has been calibrated using carbon-14 dates of ground-water age. Mass-balance calculations presented in the paper show the dominant reactions in the ground-water system are carbonate dissolution and cation exchange. Extremely oxidizing conditions occur in the aquifer, which provide an environment conducive to large concentrations of arsenic, chromium, selenium, and uranium. A summary of these results were presented at the final liaison committee meeting for the Central Oklahoma aquifer project.

A workshop was held for about 25 researchers interested in modeling multicomponent solute transport incorporating geochemical reactions. Reaction-transport modeling was identified as one of the most important research endeavors because it is applicable to contamination problems and because it synthesizes research from the disciplines of geochemistry, organic chemistry, ground-water flow, solute transport, and microbiology.

The program NETPATH was published. It is the latest in the series of BALANCE programs and the first to model carbon-14 ages and stable isotope evolution.

Work with Pierre Glynn on solid solutions has been accepted for the proceedings of Water-Rock Interactions-7. Formation of solid solutions is an important process in the migration of radionuclides.

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Nordstrom, D.K., Plummer, L.N., Langmuir, Donald, Busenberg, Eurybiades, May, H.M., Jones, B.F., and Parkhurst, D.L., 1990, Revised chemical equilibrium data for major water-mineral reactions and their limitations, *in* Bassett, R.L., and Melchior, D., eds., Chemical modeling in aqueous systems II: Washington, D.C., American Chemical Society Symposium Series 416, p. 398–413.

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TITLE: Chemical Modeling and Thermodynamic Data Evaluation of Major and Trace Elements in Acid Mine Waters and Ground Waters (CR 92-326 (formerly WR 75-128))

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PROBLEM: Aqueous chemical models have become popular tools for the interpretations of natural water chemistry. Unfortunately, these models have deficiencies because of (1) incorrect or inconsistent thermodynamic data, (2) invalid assumptions regarding the equilibrium state, (3) inappropriate or unvalidated corrections for nonideality, (4) inadequate expressions for temperature dependence, (5) unvalidated limitations for ionic strength, composition and temperature, and (6) lack of data on solid solution solubility. The plethora of models and databases has prompted federal agencies, especially hazardous waste and nuclear waste managers, to request geochemical code validation. Acid mine waters are a major source of water pollution and provide one of the best challenges to the application of trace element speciation models.

OBJECTIVE: Develop, test, validate and make field applications of chemical models for equilibrium speciation and mass transfer of major and trace constituents in acid mine waters and ground waters.

APPROACH: (1) Compile and evaluate physical and chemical data for individual constituents and for reaction equilibria pertinent to natural waters. (2) Test applicability of current models to interpret natural water chemistry in acid mine waters and ground waters in field situations. (3) Identify limitations of current models in terms of ionic strength, composition, temperature and inhibitions to equilibrium. (4) Develop a chemical model based on mean activity coefficient data and reliable reaction equilibria to evaluate relevant chemical reactions in natural waters over a wide range of ionic strength. (5) Test the equilibrium assumption of current or new models against field data where both water and mineralogical analyses can be obtained. (6) Measure mineral solubilities or other reaction equilibria in the lab or in the field where necessary data are lacking from the literature.

GROUND-WATER CHEMISTRY

PROGRESS: (1) Qualitative chemical modeling on ground waters from the International Stripa Project has been completed and a first draft has been completed. Editing and revision is underway. (2) The most extreme example known of acid mine waters has been sampled at the U.S. Environmental Protection Agency (EPA) Iron Mountain Superfund Site for which the project chief is a key advisor. Values of pH range from 0.5 to -3.0 or less. Papers are being prepared for scientific interpretation and to assist the EPA in their management of the site. (3) A major report on a comparison of analytical techniques for the determination of metals in acid mine waters has been submitted for approval. (4) Chemical modeling of Cu, Zn and As alternative in the Leviathan acid mine waters has progressed, looking at both adsorption and precipitation reactions.

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GROUND-WATER CHEMISTRY

TITLE: Mineral-Water Interaction in Saline Environments (NR 69-020)

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PROBLEM: Saline hydrologic systems provide a wide range of conditions within which to examine hydrochemically important mineral reactions (alteration or genesis) and to define reactants and products controlling the chemical composition of many natural waters. The effects of complex reactions, in addition to simple solution and hydrolysis, are reflected in relatively gross chemical change and interaction with fine-grained sediment.

OBJECTIVE: Use saline environments to determine mechanisms and relative importance of mineralogic processes that influence the solute composition of natural waters.

APPROACH: Study in the field and make laboratory analyses of saline waters and associated deposits, mostly from surficial sites or shallow cores in selected pilot or problem areas. Separate and examine solid and solution phases by use of high-speed and gradient centrifugation, microscopy, X-ray diffractometry, and special potentiometric apparatus, as well as detailed constituent analysis of both solids and solutions. Relate composition of these materials to the hydrochemical environment, thermodynamic conditions, and structural elements of associated mineral species.

PROGRESS: The manuscript on normative and isotopic study of saline ground waters in the central Murray Basin of Australia is undergoing minor revision following technical review. The combined correlation of the two types of data indicates that a complex hydrologic system and history can be reconstructed and clarified from the chemistry of aquitard pore fluids.

Extended interpretation of constituent correlation and normative data for brines from the Salado and underlying strata at the Waste Isolation Pilot Plant (WIPP) site, southeast New Mexico was continued with Scott Anderholm of the New Mexico district. It appears that brines from fluid inclusions definitely can be distinguished from intergranular fluids in the repository horizon and there is no indication of connection with brines from below the Salado formation.

GROUND-WATER CHEMISTRY

Hydrochemical mass balance modeling utilizing a microcomputer spreadsheet has continued with Professor Carl Bowser at the University of Wisconsin and has concentrated on the effects of silicate composition in a representative range of crystalline and clastic aquifer situations. Current emphasis is on the major solute controls of reactant plagioclase feldspar, primary mafics, and product 2:1 clays.

After preliminary review, the study with Spanish colleagues and Carol Kendall on isotopes and minor elements in Madrid Basin carbonate is being revised and extended. In the laboratory, Dr. Monserrat Ingles from Barcelona investigated and is comparing Nevada samples with materials involved in clay-water reactions in basins of northeast Spain.

Salinity fluctuation and paleoclimate implications indicated by the magnesian clay mineral assemblages and cycles in lacustrine sediments from Double Lakes, west Texas, was summarized for a symposium in Saskatoon, Canada, and presented in poster for the Clay Minerals Society. Additional work is in progress on the details of the relationships between the ultrafine mineral assemblage and the bulk chemistry of this fraction.

Considerable project effort has gone into extensive instrumental and computer upgrade, plus maintenance of the x-ray diffraction apparatus, and mineralogic analysis of particulate materials for other research (and some operations) endeavors. In addition, the project has worked on methodology and assessment of pore fluid and sediment major and minor element chemical composition for other projects and to aid in advising the Office of Water Quality. With O.P. Bricker, a chapter was prepared on principal controls of natural hydrochemical composition for a book on trace elements in natural waters.

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GROUND-WATER CHEMISTRY

TITLE: Spatial Distribution of Chemical Constituents in Ground Water (NR 57–034)

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PROBLEM: Reactions and processes that control the chemical character of ground water need to be identified to predict physical and chemical changes that occur in natural and stressed environments. This project focuses on effects of these reactions in (1) regional limestone aquifers, (2) contaminated environments, and (3) coastal aquifers.

OBJECTIVE: Study hydrogeologic phenomena reactions that relate to (1) geologic processes; (2) generation, migration, and attenuation of contaminants; and (3) processes of isotopic fractionation, (4) demonstrate contributions that can be made to science by study of historical aspects, (5) demonstrate role of hydrogeology for sustainable development of this environment and water resources.

APPROACH: Design field studies for the collection and interpretation of chemical and isotopic data within the hydrogeologic framework. Select areas that are feasible to demonstrate the occurrence, extent, rate, and consequences of chemical reactions. (1) Study changes in porosity and permeability by karstification of coastal aquifers; (2) investigate the degradation and migration of organic compounds and isotopic fractionation at contamination sites and in sulfide-rich ground water; and (3) to undertake comparative studies of regional systems in order to evaluate the environmental impact on the hydrogeologic processes and geochemical reactions. This will be done primarily on the islands of the Caribbean.

PROGRESS: For the past year, this project has been devoted largely to editing books, writing review articles, organizing international symposia, and giving lectures. Field and library work were carried out for book on "Environmental Hydrogeology" and for an article on wind as a hydrogeologic agent. Papers were presented at the International Association of Hydrologists, Geological Society of America, and Water-Rock Interaction symposia. Book on hydrogeology was completed. Work was started on preparing geochemical ground-water flow models in coastal aquifers.

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GROUND-WATER CHEMISTRY

TITLE: Interface of Paleoclimatology and Aquifer Geochemistry (NR 74-041)

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PROBLEM: Reconstructions of continental paleoclimates of the Pleistocene Epoch have relied almost exclusively on packrat midden, lacustrine, and speleothem records; such records are typically discontinuous and (or) are difficult to date. The isotopic (deuterium, oxygen-18, carbon-13) records of calcitic veins marking the sites of fossil ground water discharge, have not been utilized. Preliminary work indicates that such veins contain continuous records of Pleistocene paleoclimate and paleohydrology. The paleohydrologic interpretations should also be pertinent to selection of sites for the disposal and long term isolation of toxic wastes.

OBJECTIVE: (1) Infer paleoclimate and paleohydrology of selected regions based on variations in isotopic content of calcitic veins of ground water origin; (2) attempt correlation of inferred local variations in continental paleoclimate with global variations deduced from marine and polar ice core studies; (3) differentiate between, and determine relative magnitude of, summer and winter recharge to major uplands.

APPROACH: Sample: (1) water from regional aquifers for which quantitative hydrogeologic and geochemical studies have been completed; (2) rain, snow, snowmelt, and springs in major upland recharge areas; (3) calcite veins at modern and fossil springs. The water and calcite deposits will be analyzed for D, ^{18}O, ^{13}C, and will be dated using the TIMS U-Series methods. Initial work will be in the southern Great Basin where a major fossil spring discharge area (with a modern analogue, the Ash Meadows region) has been exhumed by uplift and erosion.

PROGRESS: Analysis of our 500,000-year oxygen-18 record from Devils Hole was completed and published by Science. Our principal findings: 1. Major climate changes in the northern and southern hemisphere were synchronous, 2. Peak interglacial climates lasted at least 20,000 years, or twice as long as indicated by marine records. 3. The so-called 100,000-year cycles are aperiodic, and actually increased in duration from 80,000 to 130,000 years during the past 500,000 years. 4. Orbitally controlled variations in solar insolation did not trigger major climate shifts during the Pleistocene Epoch; that is, the Milankovitch theory has no predictive power in the time domain.

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GROUND-WATER CHEMISTRY

TITLE: Kinetics and Thermodynamics of Chemical Evolution in Ground-Water Systems (NR 76–056)

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PROBLEM: The responsible use of our Nation's ground-water resources requires an ability to predict changes in water quality as a result of human impacts. Prediction of chemical quality in the ground-water environment depends on a detailed understanding of both chemical and hydrologic processes. To determine the spatial and temporal variability of ground-water quality, it is necessary to identify reactions occurring in the system, to define their kinetic and thermodynamic properties, and to determine how the configuration of the hydrologic regime influences ground-water quality.

OBJECTIVE: (1) Identify chemical reactions in ground-water systems using observed chemical and isotopic composition of dissolved solutes and minerals; (2) develop geochemical models to aid in interpretation of chemical and isotopic data from ground-water systems; (3) develop tools for age-dating groundwaters; (4) determine rates of chemical reactions in ground-water systems from field hydrochemical data and modeled water-ages; (5) conduct laboratory experiments to obtain thermodynamic data for mineral-water systems for use in geochemical models; (6) obtain laboratory kinetic data on rates of mineral dissolution and precipitation for comparison with field rates and (7) study the fundamental mechanisms of mineral dissolution and precipitation as they apply to pure phases and to solid-solution minerals.

APPROACH: Flow paths in ground-water systems are sampled extensively for chemical and isotopic composition. Geochemical mass balance calculations are used to interpret reaction possibilities, test reaction sensitivity to stable isotope data for aquifer minerals and dissolved solutes, and to obtain adjusted carbon-14 water ages. Rates of reactions are calculated from modeled mass transfers and water ages. Tools developed for age-dating of groundwaters include interpretation of chlorofluorocarbon (CFC) content in recharge areas and unconfined aquifers. Mathematical models are developed to (1) calculate speciation and thermodydnamic properties of a wide range of water compositions from dilute to highly saline formation waters, (2) model water-rock evolution, (3) test sensitivity of chemical evolution to advection and hyrodynamic dispersion in ground-water environments, and (4) model dissolution and precipitation reactions for water-rock systems containing solid-solution minerals. In the laboratory, synthetic solid-solution minerals are prepared using constant composition, constant growth-rate techniques. The stoichiometric solubilities of solid-solution minerals are measured to estimate the thermodynamic mixing properties of the minerals. Laboratory kinetic studies are conducted to investigate (1) fundamental mechanisms of dissolution and crystal growth of rock-forming minerals in relatively pure water-rock systems and (2) the effects of added inorganic and organic solutes on mineral-water reaction kinetics in hydrochemical environments.

PROGRESS: Detectable concentrations of Chlorofluorocarbons (CFCs, F-11 and F-12) were observed in ground water of the Snake River Plain aquifer at the Idaho National Engineering Laboratory (INEL) and in the unsaturated zone air. The INEL ground waters contain "natural" concentrations of CFCs with model recharge ages of 4 to more than 50 years; most waters having recharge ages of 20 to 40 years indicating flow velocities in the upper part of the Snake River Plain aquifer at INEL of approximately 1 m/day. Ground water near the Radioactive Waste Management Complex (RWMC), the Test Reactor Area (TRA), and the Idaho Chemical Processing Plant (ICPP) is highly contaminated with CFCs. Plumes of F-12 south of these three sites are similar in size to the tritium plumes. The unsaturated zone air is highly contaminated with CFCs near the RWMC where there is a net flux of CFCs to the atmosphere. Unsaturated zone CFC profiles at TAN show natural (uncontaminated) diffusion gradients. Ground water CFC concentrations are not in equilibrium with deep unsaturated zone air at INEL and appear to have rapidly recharged locally. Most CFC model ages based on F-11 and F-12 from 109 shallow piezometers in unconsolidated sands of the Delmarva (Delaware, Maryland and Virginia) peninsula agree within 3 years. Ground water depth/age ratios range from 1 to 2 feet/year at 29 multilevel sampling points on Delmarva. Tritium distribution on Delmarva is consistent with dispersivities of 0.1 to 2 m. Numerical simulations indicate that hydrodynamic dispersion comparable to that observed for tritium could cause F-11 ages to appear younger than F-12 ages by 5 or more years in waters recharged prior to 1960. F-11 ages are consistent with this prediction for waters with F-12 ages older than 1960, but the differences could also be due to trace F-11 contamination from well construction materials or water sampling equipment. Preliminary tritium/helium-3 and krypton-85 ages from Delmarva ground waters are in close agreement with the CFC ages. Analytical capabilities were extended to F-113, and the gas chromatographic system used to measure dissolved nitrogen and argon for definition of recharge temperatures was significantly improved. Chlorofluorocarbon concentrations have been mapped in a cross section in northern Delmarva, and used to map the age of nitrate contamination from agricultural use. Extensive sampling for CFCs in ground water was conducted at Valdosta, Georgia, Mirror Lake, New Hampshire, and in parts of north and central Florida. Unsaturated zone air was sampled at Yucca Mountain, Nevada Test Site, Nevada. Ground waters from the Pinal Creek Toxic Waste site were sampled and analysed for F-11, F-12 and dissolved gases.

F-11 concentrations are being used to age-date both contaminated and uncontaminated groundwaters at the site while F-12 measurements provide an indicator of groundwater contamination. Unsaturated-zone gas (CO_2, O_2, N_2, Ar, F-11, F-12) was collected for both chemical and ^{13}C analysis. Preliminary results show a linear CO_2 gradient, with high concentrations near the water table, decreasing toward the ground surface. Together with the very high CO_2 partial pressures measured in ground-water samples, these measurements point to the importance of carbonate dissolution in the neutralization of the acidic ground-water plume. The results enable the estimation of CO_2 exsolution fluxes from the groundwater for incorporation into a solute transport model of the site. ^{13}C values at ground surface and close to the water table show an exact difference of 4.4 per mil, which is the fractionation theoretically predicted assuming a steady-state diffusion model. Until now, there has been little field evidence supporting this theoretical model, so this result is exciting although preliminary. Solute-transport modeling of the Pinal Creek site is in progress. Because of the complexity of the occurring physical and chemical processes, the site offers a major challenge to existing reactive solute transport codes. The site is being used for intercomparison and verification of existing public-domain codes. A sensitivity analysis is also being conducted to identify chemical and physical assumptions which can be made together with code modifications and improvements needed for a satisfactory model of the Pinal Creek site and more generally any acidic ground water contamination site. A reaction kinetics capability was added to the PHREEQM geochemical transport code and preprocessor and postprocessor computer programs were also completed to facilitate use of PHREEQM. The NETPATH geochemical modeling code was published. Modifications and enhancements to NETPATH continue. The code was used to radiocarbon date ground water from the Floridan aquifer in parts of Georgia and Florida. Glacial-age paleowaters were identified that record enrichment in stable isotope composition at glacial maximum. The observation is being used to interpret paleoclimatic conditions in the southeast coastal plain at glacial maximum.

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TITLE: Physical Chemistry of Stable Isotope Fractionation in Hydrologic Processes (NR 75-064)

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PROBLEM: Several light stable isotopes (H, C, N, O, Si, and S) show variations in their isotope abundances and offer great promise for study of evaporation, ground-water mixing, biotransformations, lake or reservoir circulation and stratification, and associated hydrochemical phenomena. These isotope fractionations are related to: (1) purely physical processes; (2) heterogeneous chemical equilibria; and (3) reaction kinetics. Many of these processes are not sufficiently understood or quantified to make the most effective use of stable isotope techniques in hydrologic research.

OBJECTIVE: Develop theoretical and instrumental mass spectrometric techniques through experimental investigation, and test in suitable field locations, such as intermontane ground-water reservoirs, closed-lake basins, and suitable surface reservoir, lake, ground water, or estuarine systems, to aid in more complete utilization of light stable-isotope phenomena in hydrologic studies.

APPROACH: Water and mineral samples from experimental studies, from evaporating surface water bodies, and from ground-water basins, will be analyzed for light stable isotope abundances. These experimental results and field data will then be related to to other measurement factors such as relative humidity, temperature, density, and water chemistry, in an attempt to develop an understanding and a theoretical predictive model of the processes involved.

PROGRESS: Nitrogen isotope and ground-water dating studies have been initiated by J.K. Böhlke in several field areas by collaboration with district hydrologists and in conjunction with the Toxics Program and the National Water Quality Assessment Program. These projects are designed both (1) to evaluate the use of different geochemical and isotopic tools in diverse settings, and (2) to determine the fate of nonpoint source nitrate contamination in a variety of ground-water/surface-water systems. In support of these projects, the nitrogen isotope laboratory has produced relevant data for a variety of soil and organic solids, dissolved ammonium, nitrate, and nitrogen gas in waters, and nitrogen in mixed gases. We also continue to work closely with the ground-water kinetics project to develop and test applications of chlorofluorocarbon (CFC) recharge dating.

One such study was completed on the Delmarva (Delaware, Maryland, and Virginia) Peninsula to document the fate of ground-water nitrate contamination in small agricultural watersheds. The study demonstrated the combined use of nitrogen isotope ratios and ground-water recharge ages (estimated from CFC analyses) to resolve the effects of changing agricultural inputs and subsequent chemical transformations along ground-water flow paths. With additional chemical and carbon isotope data, it was concluded that: (1) The nitrate concentrations of ground waters leaving the water table have increased by an order of magnitude since 1950; (2) Nitrate is relatively stable in ground waters in the surficial sandy aquifer; (3) First- and second-order streams are receiving discharge of ground waters that recharged in the period 1940–1975 and had low to moderately elevated nitrate concentrations when they were recharged; (4) Some streams are receiving discharge of unmodified nitrate-contaminated ground waters, whereas other streams are partially shielded from nitrate contamination by denitrification zones.

Tritium data were collected by R. Michel from the Regional Aquifer System Assessment (RASA) site in Ventura, California. These data confirm a recharge rate for the upper aquifer of approximately 2 meters/day from the Saticoy spreading fields. The spreading fields are not effective in recharging the lower aquifer. Saline waters intruding the aquifer near the coast have no measurable tritium in most cases, indicating that the saline water is not derived from recent seawater. Only a shallow well located within 100 yards of the shore line contained post-bomb tritium.

Tritium concentrations in the Finger Lakes of New York are related to the expected turnover time of the lakes. Estimates of the residence times of the waters in the individual lakes are being calculated by R. Michel.

Preliminary soil core data indicates that tritium will be a useful tracer for movement of irrigation water through the unsaturated zone at the Minnesota Management System Evaluation Area (MSEA) site.

A scintillation counting system has been calibrated by R. Michel to analyze sulfur-35, and analysis of samples will begin this year.

Accepted for publication in Science is a paper that shows that oxygen isotope ratio profile of calcite vein core DH-11 from Devils Hole, Nevada (over the period 500 to 50 thousand years ago), mimics the Vostok Antarctic ice core record and indicates that orbitally controlled variations in solar insolation could not have been a major factor in triggering deglaciations during this period.

Carbon-13 content in this core is inversely correlated with oxygen-18 abundance. Although carbon exchange is an important process in this system, we now attribute variations in carbon-13 content to (1) variations in area and density of vegetation in the major recharge area and (2) possibly to variations in global carbon-13 abundance.

Working with M.J. Baedecker, K. Revesz has employed carbon and hydrogen isotope ratios of methane in the saturated zone, the unsaturated zone, and the atmosphere at the toxic waste site at Bimidji, Minnesota. They find that methane is produced by a fermentation pathway. They were able to calculate methane consumption based on methane concentration and isotopic composition.

Chemical and isotopic analyses of fluid inclusions were completed by J.K. Böhlke with co-workers at the University of California. A series of papers were published that describe a new micro-analytical method and its applications to understanding sources of water, sources of fluid salinity, mixing, and boiling processes in a variety of "fossil" geothermal systems. For example, new data indicate that the brine responsible for some fluorite deposits in central New Mexico began as fresh meteoric water, acquired salinity by dissolving evaporite deposits in the subsurface, acquired lead and radiogenic noble gases from interactions with clastic sedimentary rocks, and then precipitated fluorite without having boiled.

Using the gaseous hydrogen-water equilibration system published last year, we were able in a cooperative study with the National Institutes of Health to demonstrate that this technique analyzes urine samples from diabetes patients for deuterium content with significantly greater precision than standard techniques. The standard techniques heat urine samples above 400 degrees Celsius to convert hydrogen of water to gaseous hydrogen, but glucose is also converted, leading to analytical error. This difficulty is eliminated in the equilibration technique because hydrogen in glucose is not exchangeable at the equilibration temperature of 30 degrees Celsius.

Stable isotope reference samples are of critical importance in laboratories around the world and they have not received sufficient attention during the past few years. Project personnel homogenized and bottled several hundred to a thousand aliquots of a new graphite material and two new ammonium sulfates. Working with colleagues from the National Institute of Standards and Technology (NIST), reports of investigation were prepared for 23 light stable isotope reference materials. These will be distributed by the International Atomic Energy Agency in Vienna and NIST in Gaithersburg, Maryland.

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GROUND-WATER CHEMISTRY

TITLE: Chemical Models of Natural Systems (NR 79-093)

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PROBLEM: The increasing need for understanding the effects of human activity on the chemistry of natural systems requires a continually increasing degree of sophistication in the models used to describe the processes through which these effects occur. Such models include thermodynamic and (or) kinetic models of aqueous speciation, the chemistry of dissolved gases, gaseous and aqueous diffusion, transport of constituents across interfaces, redox processes, mineral-water interactions, the chemistry of anthropogenic inputs to natural systems, and isotope effects associated with these processes.

OBJECTIVE: (1) Identify the factors influencing the reactions and transport of solutes in natural waters; (2) evaluate reactions and transport processes for volatile constituents in unsaturated zones; (3) identify processes occurring at the interface of the saturated and unsaturated zones (the capillary fringe); and (4) investigate the application of isotope effects as a tool for understanding these processes.

APPROACH: (1) Conduct field studies at sites selected for investigation of particular processes; (2) analyze gaseous and (or) dissolved constituents (and their isotopes) as needed; (3) develop theoretical reaction and (or) transport models for specific processes under investigation; and (4) apply these theoretical models to natural systems.

PROGRESS: The progress on Yucca Mountain geochemistry is more evolutionary than discrete in terms of accomplishments, and the mountain continues to confound. The expected decrease in carbon-14 in the 1991 UZ6 samples was not observed; instead a slight increase occurred. Nevertheless, the deep borehole gases retain a consistently distinct carbon-14 signature from the gases in the shallow system for two successive annual samplings, in spite of the fact that the general CO_2 content and carbon-13 signatures of the gases in the two systems are nearly identical. Thus, even in the presence of a deep, large-diameter borehole, the carbon-14 content of gas in the shallow and deep systems remain distinct. The implication thus continues to strengthen that the carbon-14 differences are due to age. There is still no evidence that the observed differences can be attributed to reactions; thus it seems plausible that the principal retardation of any carbon-14 dioxide that may escape the proposed repository might by physical, rather than chemical, in origin.

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TITLE: Dispersion of Toxic and Radioactive Wastes in Ground-Water Systems (NR 81-122)

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PROBLEM: Movement of toxic and radioactive substances in aquifer systems occurs in all gaseous, liquid, and solid phases and is controlled by hydrologic and chemical forces. Solute movement can be greatly affected not only by physical dispersion but also by other factors such as exchange, sorption, chemical kinetics, and ionic distributions. Movement of gases and particulate material in the unsaturated zone is controlled by many additional factors. Knowledge of how these physical and geochemical factors affect prediction of movement of toxic and radioactive wastes is only generally known for ideal systems.

OBJECTIVE: Develop field methods and techniques that will yield values for physical and geochemical factors of regional significance in a ground-water system.

APPROACH: Undertake studies in which appropriately developed field methods and techniques are applied to stressed systems. Define the importance of the various factors and find a means for measuring the magnitude of each.

PROGRESS: A series of two papers by W.W. Wood and W.E. Sanford on the relationship of ground water leakage to the solute chemistry of topographically closed basins has resolved a long standing problem on the assemblage and thickness of evaporite mineral found in these basins. The proposed model provides a rational for economic exploration of commercially valuable evaporite minerals in addition to the understanding of the physics and chemistry of a complex hydrologic system. It was found that the rate of ground-water leakage from the basin was as critical to the development of the mineral thickness and mineral assemblage as was the solute chemistry of the input water.

W.W. Wood and W.E. Sanford, working at Double Lakes, a topographically closed basin near Tahoka, Texas, have identified and quantified a significant chemical flux leaving the basin by eolian processes. On an annual basis more than two-thirds of the chloride entering this basin from ground water and surface water sources is removed by wind blowing the fine surface evaporites out of the basin. Water management aspects of this finding are significant. It had been previously assumed that the ground water solute plumes that exist down gradient from the many saline lakes in the Southern High Plains were the result of brines entering the aquifer from lower formations. Field work was conducted in Australia to evaluate the processes observed in Texas in an analogous, but much older, hydrogeologic environment.

W.W. Wood, W.E. Sanford and C.C. Reeves (Texas Technical University) offered a new model for the origin of large lakes basin in the Southern High Plains of Texas and New Mexico. This model suggests that high levels of ground water prevented the development of calcrete in the vicinity of bedrock highs. Without a calcrete cover eolian processes were able to erode the uncemented areas. This model offers a viable explanation for the universal association of these basins with bedrock highs. Previous analyses of these basins suggested they resulted from dissolution of underlying bedded salt and consequence collapse which would imply that they should be associated with bedrock lows.

Work continues on collection of water samples for solutes and isotope analyses of the Survey's fractured rock research site near Mirror Lake in New Hampshire. Emphasis this year has been collecting and analyzing water samples from very low permeability fractures.

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TITLE: Comparative Study of Organic Degradation in Selected Hydrogeologic Environments (NR 83-129)

PERSONNEL: Mary Jo Baedecker, Project Chief
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PROBLEM: Degradation of organic material produces organic compounds that both alter the quality of water and affect the inorganic reactions. The hydrogeologic controls on organic-inorganic reactions, their rate, and progress are not well understood. This project focuses on the occurrence and fate of organic compounds in (1) contaminated aquifers, (2) soils, and (3) lake sediments.

OBJECTIVE: Increase our understanding of reactions involving organic matter and to evaluate the significance of these reactions in geochemical studies. Specific objectives are (1) to identify organic and inorganic compounds that are present as a result of the degradation of organic material; (2) to study the interaction of organic compounds with soil and aquifer materials; and (3) to develop geochemical models in organic-rich environments.

APPROACH: Several organic-rich environments with chemical and hydrologic background data will be selected from which samples can be obtained and analyzed for organic and inorganic constituents. In these areas, where degradative processes are primarily anaerobic, the extent and effects of chemical reactions and processes will be investigated. Of interest is the type of organic material present, the interaction of organic compounds with sediment, the migration of organic compounds, the fractionation of isotopes and generation of gases, and the fate of inorganic constituents in association with organic material.

PROGRESS: Field investigations and laboratory experiments were conducted to understand processes in two shallow sand and gravel aquifers contaminated with petroleum products. Work continued on identifying the nature of the organic compounds dissolved in ground water and the controlling biogeochemical reactions that occur in contaminant plumes downgradient from hydrocarbon sources. An open-loop stripping method was compared to a microextraction technique for the analysis of monoaromatic hydrocarbons. The open-loop stripping method yielded results that are more variable, but with a greater sensitivity and specificity compared to the microextraction technique. Monoaromatic hydrocarbons were transported downgradient from the sources at both field sites. Biodegradation and physical processes controlled the concentrations and distribution of the hydrocarbons in ground water. Organic acids (aliphatic and aromatic monocarboxylic acids) that are transformation products from the microbial oxidation of hydrocarbons were identified in the contaminant plumes. High concentrations of organic acids were associated with hydrocarbons in the anoxic plumes where reduction of sulfate, nitrate, and iron and methanogenesis occur. Changes were found in the concentration and composition of the organic acid pool with time. Water-rock interactions also were investigated at the two sites. Several authigenic minerals that form in near-surface environments were found where organic compounds are degrading.

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TITLE: Relationship Between Chemical Quality of Natural Waters and Human Health and Disease (NR 79–132)

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PROBLEM: In recent years, there has been increasing interest and study concerned with the possible relations between the chemical quality of natural waters and human health and disease. Medical researchers recognize areal patterns of health and disease in the United States and suspect that these patterns may be controlled by environmental and nonenvironmental factors. After excluding nonenvironmental factors, local and regional differences in water quality appear to have an effect on health and disease. Such differences influence the total dietary intake of necessary major and trace elements and the concentration of certain potentially toxic chemical constituents.

OBJECTIVE: Discover and quantify relations between the chemical quality of natural waters and human health and disease.

APPROACH: Identify chemical constituents in natural waters that are most likely to affect health and disease and those medical conditions most likely to be affected by water quality. Determine the temporal and spatial associations between specific chemical characteristics of water and specific states of health and disease. Exclude known high-risk factors related to geographic areas (for example, urban environment, mining activity) to increase the likelihood of detecting risk factors associated with natural water quality. Initially, use existing data from sources such as the U.S. Geological Survey and the Bureau of Vital Statistics for the medical and hydrologic aspects of the study. Collect new data in the field if data are lacking. Supplement data collection through cooperative programs with District and aquifer-study water-quality specialists. Obtain information on chemical composition of soils, rocks, and plants through cooperation with the Branch of Regional Chemistry, Geologic Division. Cooperate with Dr. Howard C. Hopps, Curators Professor of Pathology, University of Missouri Medical School, throughout this study.

PROGRESS: Determined that Pliocence liqnites may be the source of organic compounds contributing to Balkan Endemic Nephropathy (BEN) in Yugoslavia, Bulgaria, and Romania. Aniline and Polycyclic aromatic hydrocarbons seem the most likely compounds to be implicated in BEN. Work with Dr. Philip Hall (Nephrologist, Case Western Reserve University, Cleveland, Ohio,) and Dave Wolf (National Mapping Division) indicates that there are restricted geographic areas in the United States with kidney mortality from disease patterns similar to BEN. Further work on BEN and other diseases has led to a planning meeting between USGS-WRD, NMD, and the national Center for Health Statistics for a possible future project. Further work in the Great Hungarian Plain containing ground water drinking supplies with very high nitrate indicate that there may be an increased incidence of gastric cancer in these areas.

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TITLE: Uranium-Thorium Series Radioisotopes in Ground-Water and Surface-Water Systems (NR 82-138)

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PROBLEM: Naturally occurring uranium and thorium series radioisotopes possess great potential as natural tracers for examining movement and mixing of water bodies. At present, however, not enough is known of their geochemical behavior to be used even semi-quantitatively for this purpose. In addition, new analytical techniques are being developed which will allow determination of isotopes of chlorine, krypton, iodine and other elements. These isotopes will also be of use in the hydrologic sciences as tracers, if sufficient understanding of their geochemical behavior can be achieved.

OBJECTIVE: Learn enough about the geochemical behavior of uranium and thorium series radioisotopes to permit their use as naturally occurring tracers to solve hydrological problems. Keep abreast of developments in the field of chlorine, krypton, iodine, and so forth, geochemistry and isotope analysis for possible application to hydrologic sciences.

APPROACH: Studies of uranium and thorium series radioisotopes will be carried out in a variety of well known surface and subsurface conditions and their behavior related to specific physical and chemical conditions and processes. Laboratory studies will be carried out as needed under carefully controlled conditions to examine specific aspects of behavior. When behavior of these radioisotopes is well known, these principles can be applied to hydrologic problems of less well-defined systems to determine if methods developed can contribute answers which are at least reasonable with respect to results from other hydrologic approaches. As confidence is gained through these processes, methods will be applied to poorly constrained hydrologic problems not amenable to solution by standard hydrologic techniques.

PROGRESS: All 11 Finger Lakes in Central New York State were sampled for radium isotopes, tritium, and stable hydrogen and oxygen isotopes. This sampling will allow an intercomparison of age estimates of the water in the lakes based on known historical trends of tritium in precipitation and the radium isotopic method, which is the focus of this effort. Comparison of the results of these two methods will reveal much about sources of water in the lakes and chemical processes taking place in the lakes; for example, where and how much groundwater is coming into the lakes, whether element removal is taking place in the lakes over the course of a year, and whether radium diffuses from bottom sediments into the overlying lake water.

Also during this year, a study was completed demonstrating the use of radium isotopes in solving hydrological problems, such as determining stream-mixing proportions, estimating ground-water inflow into streams, and identifying the source of spring water based on radium isotopes. The study area was around Rapid City, South Dakota. A paper is in preparation describing this work.

A network of uranium sampling stations has been set up on the major rivers draining the United States mid continent. This sampling network will be used in long term studies to examine seasonal fluctuations of uranium and obtain an accurate flux estimate of uranium to the Gulf of Mexico. The amount of uranium added to farmland in the United States mid continent with phosphate fertilizer also has been calculated for comparison with the river flux.

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GROUND-WATER CHEMISTRY

TITLE: Transport and Biogeochemical Fate of Organic Substances in Aquatic Environments (NR 91-151)

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PROBLEM: Organic substances are transported in both particulate and dissolved phases in aquatic environments. However, our understanding of the processes affecting phase exchange and removal are incomplete. In order to predict the short- and long-term fate of toxic organic substances in a variety of aquatic environments, it is necessary to determine the physical properties of these compounds and establish kinetic data on their removal rates using a combination of field studies and laboratory experiments.

OBJECTIVE: The objective is to investigate the composition and concentration of organic matter associated with dissolved and particulate phases in surface and subsurface waters and compare these data with distributions based on laboratory partitioning experiments and physical partitioning (for example, fugacity) models. I wish to develop data on data on the rates at which organic matter is transformed (and remineralized) and the products that result in aquatic environments. This information will be used to establish the relative importance of different removal processes under a variety of environmental conditions. Ultimately these results will be incorporated into particle and solute transport models.

APPROACH: Studies will be carried out at one or more field sites that present favorable opportunities for examining the transport and fate of organic contaminants in different aquatic environments. Particulate and dissolved phases will be analyzed for the presence and concentration of a variety of natural and anthropogenic organic substances and their variation over time. Experiments will be performed in the laboratory to determine the equilibrium phase partitioning, desorption rates and biodegradation potential (and rates) of selected organic compounds. These equilibrium and kinetic data will be compared with the results of field studies and models that predict physical partitioning.

PROGRESS: During Fiscal Year 1992, my activities have been dominated by my participation in the National Oceanic and Atmospheric Administration (NOAA)-sponsored coastal contamination

contamination study. In the remaining time, I have prepared and submitted for publication two manuscripts (to the Journal of Chromatography and Applied Geochemistry) that describe the analytical methods and results obtained by me and my co-workers at the Bemidji, Minnesota, oil spill site. In addition, I am coauthor on another paper submitted to Applied Geochemistry on the coupling of the inorganic and organic geochemistry at this site. I am also a coauthor on a paper presently in press to be published in the Journal of Chemical and Engineering Data. This paper describes the physical properties (for example, vapor pressure, log Kow and aqueous solubility) of the long-chain linear alkylbenzenes. I have completed a large chapter (ca. 250 p.) on Chemical Oceanography and Geochemistry to be published in a book entitled, "The Ecology of the Southern California Bight" (University of California Press). The galley proofs are expected any day. Finally, I have completed final revisions on a report to the State of California on field studies in support of a modeling project which aims to characterize the deposition of wastewater particles on the continental shelf off southern California. I have also been assisting NAWQA and the Central Lab with their efforts to better define and ultimately develop state-of-the-art analytical procedures for determination of polychlorinated biphenyls (PCB) in a variety of matrices.

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GROUND-WATER CHEMISTRY

TITLE: Factors Determining Solute Transfer in the Unsaturated Zone (WR 68–036)

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PROBLEM: Quality of ground and surface waters often is influenced significantly by chemical and solute-dispersion processes of the unsaturated zone. Frequently, these influences are impossible to predict because the effects of certain relevant, unsaturated-zone factors (for example, changes in water content or in the nature of solid surfaces) are understood imperfectly and because the current transport-modeling methods may not be well adapted to the situations encountered in practice. As a result, it may be impossible to assess properly the availability and quality of a given water resource or to predict the effects of certain human activities or management practices upon such water quality.

OBJECTIVE: Develop and test theories and mathematical models of reacting-solute transport to enhance the usefulness of such theories and models for assessing the effects of solute transport in the unsaturated zone on water resources and environment quality. Include in the study chemical reactions involving radioactive nuclides as well as reactions of certain solutes found in industrial and agricultural effluents. Develop mathematical models aimed at managing subsurface water quality.

APPROACH: Develop new mathematical models to predict transport of reacting solutes through porous media or at media boundaries, with consideration of the special conditions encountered in the unsaturated zone. Use theory, numerical methods, and controlled experiments. Use the interaction between theory and experiment to enhance the understanding of processes involved. Stress unidirectional transport. Study water-saturated systems with slow, steady water flows and a single, primarily equilibrium-controlled chemical reaction; study steady but unsaturated flows, paying special attention to the influence of water content on chemical and dispersion parameters; and study fast, perhaps transient, flows and chemical-kinetics influences and interactions among several reactions. Develop ground-water pollutant management models that combine numerical-simulation models and management techniques such as linear programming. Initially focus on pollutant-source management in transient one-dimensional systems with linear chemistry. Subsequently, investigate pollutant-source management in two dimensions with nonlinear, one-component chemical systems. Use existing simulation models and management models to enhance joint management and simulation capabilities.

PROGRESS: Continued studies of the release of polychlorinated biphenyls (PCB) from sediments in the Lower Fox River in Wisconsin (in cooperation with John Elder, Wisconsin District). Distribution of PCB between water and sediment phases has been studied in the laboratory using short, saturated, flow-through columns at a variety of water flow rates. Distribution coefficients are similar to previously reported values and the distribution between phases appears to be equilibrium controlled and is not affected by flow rate. Sediment samples from three depths at two sites have been studied using one PCB congener and native river water. Carbon-14 labeled PCB is used to facilitate analyses.

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TITLE: Partitioning of Solutes between Solid and Aqueous Phases (WR 70–065)

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PROBLEM: When solutes are introduced into a ground-water system or into surface waters, physicochemical reactions can occur between the dissolved solutes and native solid materials. Detailed knowledge of the chemical reactions that occur at solid surfaces is required to assess the effects of such inputs on water quality. In addition, the geochemical cycling of some trace elements may be controlled by the distribution between solid and aqueous phases. A fundamental understanding of the surface-chemistry reactions is needed to incorporate a mathematical description of these processes into chemical-equilibrium and solute-transport models.

OBJECTIVE: (1) Study the adsorption behavior of inorganic and organic solutes on particulate materials that are important in natural systems, including aluminosilicate minerals, model colloids (such as hydrous oxides of aluminum, silicon, iron, or manganese), and solids of biogenic origin; (2) derive stability constants for the partitioning of solutes between a particular solid surface and the aqueous phase and understand the mechanisms of surface bonding from a theoretical perspective, including electrical double-layer theory; and (3) generate a surface-stability-constant data base that is compatible with existing computer models of chemical equilibrium and that could be used in the field evaluation of solute-transport models.

APPROACH: (1) Conduct experiments in the laboratory, of physical-chemical techniques to characterize surfaces and to measure adsorption behavior as the type of solute, type of surface, and water composition are varied; (2) use controlled laboratory solutions in both kinetic and equilibrium studies to evaluate the importance of surface reactions for a given solute in a given geochemical environment; (3) develop quantitative phenomenological models to describe observed laboratory results and predict the behavior of solutes under other experimental conditions with the aid of a computer; and (4) conduct field studies periodically to assess the applicability of the models to natural aqueous systems.

PROGRESS: Progress was made in laboratory and field studies of chemical processes influencing metal transport in the shallow aquifer at the Cape Cod Toxics Substances Hydrology research site. Laboratory studies have shown that Cr(VI) is reduced in the aquifer primarily by reaction with Fe(II) in fine-grained material (less than 64 microns), which represents only one percent by weight of subsurface material. A one-dimensional, rate-controlled solute transport model was developed with J. Friedly of the University of Rochester that accurately simulates both laboratory reaction data and field transport data for Cr(VI). In the field, the rate is controlled by diffusion to reaction sites in immobile fluid regions. A laboratory study of the spatial variability of Pb and Zn adsorption at the site shows that metal ion adsorption varies by less than a factor of 3 (under constant conditions) for samples at the field scale (100 meters).

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TITLE: Stable Isotope Tracers of Biogeochemical and Hydrologic Processes (WR 91-080)

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PROBLEM: Light stable isotopes such as oxygen, hydrogen, carbon, nitrogen and sulfur have proved to be extremely useful tracers of hydrologic pathways and biogeochemical processes. However, use of these isotopes as tracers is presently hampered by our limited understanding of the physical processes and chemical reactions influencing isotopic compositions. The unsaturated zone, particularly the soil zone and the top of the water table, is probably the portion of the hydrologic system most responsible for alteration of the isotopic compositions of potential isotope tracers; this environmental component is also one of the least studied.

OBJECTIVE: The overall goal is to increase our understanding of reactions involving stable isotopes and to evaluate the significance of these reactions in geochemical and hydrologic modeling. This will be accomplished by field and laboratory investigations of processes and reactions which may fractionate isotopes and affect their utilization as tracers of processes, flowpaths, and sources of water and solutes.

APPROACH: Define the processes which could affect the use of isotopes as tracers; identify suitable field areas for collaborative research; develop field sampling techniques and laboratory analytical methods which do not fractionate the isotopic compositions; investigate the extent and effects of isotope exchange between gases, water, bound-water, dissolved species, and matrix materials through field studies, and laboratory and field experiments; develop conceptual models for infiltration, streamflow generation, unsaturated and saturated zone flow, and biogeochemical reactions; test biogeochemical-process and hydrologic-flow models with isotope tracers; establish guidelines for application of stable isotope techniques to problems of National importance.

variation of meteoric-derived water available for the the modern-day U.S.A. and will be an invaluable basis of comparison for paleoclimatic studies. The most striking features of the study are: (a) the robustness of the isotopic patterns seen by contouring the data on maps; (b) each locality has its own well-defined meteoric water line (MWL) with an average slope of 6, although for the entire dataset the slope of the MWL is 8; and (c) large regional areas have similar MWL slopes, suggesting regional control by local airmasses of similar humidity.

(2) Preliminary strontium isotope data confirm that carbon isotopes can be used to distinguish between sources of water at Catoctin, Maryland; the combination of C and Sr appears to be very powerful for watershed studies. Both isotopes show a much more dynamic picture of fluctuations of water sources and flowpaths over storm events than has been seen with oxygen isotopes alone. This has resulted in a major change in our view of the hydrologic behavior of the catchment.

(3) Modeling efforts at the Hydrohill (China) experimental catchment have shown that the Delta ^{18}O hydrograph separations are almost identical to unit hydrographs made for various subsurface waters and for the catchment as a whole; in contrast to most studies, at all levels the water is mostly new quickflow. Hydrograph separations made using silica and chloride, while similar to each other, suggest a much larger contribution of old slowflow. This study provides very convincing evidence of how and why chemical species make such poor conservative tracers of waters or flowpaths in watersheds.

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TITLE: Geochemistry of Water in Fine Grained Sediments (WR 76-139)

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PROBLEM: The energy potential of geothermal waters from geopressured systems is enormous. Geochemical data are necessary for delineating favorable exploration areas, estimating the recoverable geothermal resources from a given reservoir, and identifying potential pollution, waste disposal, and corrosion problems.

OBJECTIVE: To study the chemistry and controls on the chemistry of water in geothermal and other subsurface systems. Provide basic data needed to estimate the geothermal energy and other resources and to identify potential pollution, waste disposal, and corrosion problems associated with extraction of energy and other resources from these systems.

APPROACH: Collect water, gas, and rock samples from prospective geopressured and other subsurface systems for chemical, mineralogic, and isotopic analyses. Carry out membrane and water/rock interaction laboratory studies. Data analyses will be performed by available and planned computer programs.

PROGRESS: Most of the project's effort was devoted to completing the field work and the reports on geochemical investigations of hydraulic connections between the Corwin Springs Known Geothermal Resources Area and adjacent areas of Yellowstone National Park, Wyoming. In Fiscal Year 1992, two additional field trips were carried out to complete the data coverage in the Norris-Mammoth Corridor of the Park. I coordinated the geochemical aspects of this congressionally mandated study that involved scientists from three USGS projects and several non USGS geochemists. An extensive geochemical data set consisting of detailed chemical and isotopic compositions of water, solutes, gases and rocks was obtained in order to understand the origins and evolutions of waters in the area. Results are conclusive and show that waters from the Mammoth Hot Springs and La Duke Spring area have evolved chemically and isotopically by reactions with different rock types and are not directly connected. The geochemical data in general, and $^{3}He/^{4}He$ ratios in particular indicate that the Mammoth system is not directly connected to the Yellowstone caldera but may result from recent magmatic intrusions underneath Mammoth.

SOLMINEQ is a comprensive geochemical code that can be used to study water/ rock/gas interactions at temperatures of 0 to 350 degrees C. We have made additional modifications to SOLMINEQ, especially those dealing with treating solutions with high salinity and pH similar to those obtained from reacting brines from Paradox Valley, CO (Bureau of Reclamation study) with portlandite and other cements.

The interest in the 7th International Symposium on Water-Rock Interaction (WRI-7) has been tremendous. As Secretary General, I am devoted some of my time to coordinating this meeting, in July 1992. I am also the senior editor of two-volume Proceedings that contain 1686 pages.

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GROUND-WATER CHEMISTRY

TITLE: Chemical and Isotope Studies of Thermal Waters of the Western United States (WR 79–165)

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PROBLEM: Reconnaissance and chemical and isotope sampling of thermal springs in the western United States generally has not provided information of sufficient detail to permit the geothermal potential of most individual areas to be determined with any certainty. This is especially true in the Cascade Mountain Range, where the chemical geothermometers indicate much lower temperatures of water-rock equilibrium than the sulfate-isotope geothermometer and the geologic setting seem to indicate. This discrepancy could be due to simple mixing of thermal water and freshwater or rapid equilibration of water with surrounding country rock as the fluids rise to the surface; alternatively, the sulfate-isotopic composition could be an artifact reflecting the original source.

OBJECTIVE: Investigate the origin of the dissolved constituents, water, and gases discharging in hot springs and determine their relation to fumaroles and cold mineral springs. Determine the recharge areas for the thermal springs and the amount of mixing of thermal and nonthermal waters.

APPROACH: Do chemical isotopic analyses on samples of water and gas discharging from thermal, cold, and mineral springs. Use the chemical and isotopic data to determine the extent of mixing and ascertain the probable recharge areas for the individual thermal systems. Investigate the factors that control the chemical and isotopic composition of the fluids.

PROGRESS: Chloride-rich thermal waters discharged by hot springs in the Oregon Cascades are anomalous because no obvious source of chloride exists in the Late Tertiary to Quaternary continental volcanic rocks of the Cascade Range. No rocks older than Oligocene (continental volcanics) are known to exist beneath the High Cascades. However, the Na-Cl and Na-Ca-Cl nature of the thermal waters and the unusually large dissolved nitrogen concentrations indicate the presence of an organic-bearing marine rock. A new tool useful in dating old waters in

Iodine-129 (15.6 Ma half-life). Na-Ca-Cl thermal waters discharging from the Cascade Range in Oregon have Iodine-129 activities appropriate for a source rock of Eocene age. Clearly, previously unknown marine rock of Eocene age underlie at least part of the Cascade Range in Oregon and southern Washington. As an independent check on the method, formation waters discharging from marine Cretaceous units adjacent to the Cascade Range in northern California and Washington were also analyzed for Iodine-129; both samples gave Cretaceous ages.

The geothermal system at Steamboat Springs, Nevada is a classic "rhyolitic" geothermal system. We have begun a long term study of the degradation of the Steamboat Springs system with progressive development. Our initial sampling indicates that the chemical and isotopic compositions of the weakly thermal groundwater and the hot spring waters are related to the high temperature waters withdrawn by wells at the geothermal power plant by dilution, conductive cooling, steam condensation, and water-rock reaction. As additional development stresses the system, we will study (model) the chemical and isotopic changes.

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GROUND-WATER CHEMISTRY

TITLE: Chemistry of Aquatic Organic Matter (WR 84–189)

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PROBLEM: The intrusion of industrial, agricultural, and domestically produced organic chemicals and wastes into the aquatic environment is well known and is considered to be one of the most important environmental problems. The widespread distribution of these anthropogenic substances, in addition to naturally occurring organics, and their detrimental impact on the Nation's water resources points to the need to understand how these substances act and react in the environment. Knowledge of transport, persistence, transformation, solubility, sorption, and reaction kinetics is needed to determine the fate of the substances in the hydrosphere.

OBJECTIVE: (1) Identify organic substances associated with a given field problem, in aqueous and nonaqueous phases, sorbed, and in an unsaturated atmosphere; (2) chemically determine any biotic or abiotic degradation or transformations occurring in the field; (3) measure sorption and reaction equilibria and rates within the aqueous system and at the water-mineral interface from field observations and laboratory simulations; and (4) determine the behavior of organic solutes and vapors in the unsaturated zone.

APPROACH: (1) Use high-performance liquid chromatography, capillary gas chromatography, and computerized gas chromatography/mass spectrometry to make qualitative and quantitative organic analyses; (2) do sorption studies by means of column technology previously developed in this laboratory; and (3) conduct work at two field sites on organic wood preservatives, which are ground-water contaminants, and initiate work at two other field sites where the ground water is contaminated by crude and refined petroleum products.

PROGRESS: Four aquifer cores were collected at the Pensacola, Florida, site where ground water is contaminated by wood-preserving chemicals. The cores were collected in a manner that retained coexisting pore water. The samples were taken directly downgradient from the source, which, as determined in previous work, is in a reach of enhanced microbial activity. Nearly continuous core samples were taken from the land surface, through the porous sand, down to a more confining clay layer, which occurs at a depth of about 20 feet. Detailed organic analytical data are being obtained on both the water and sediment samples from this location. The samples were collected for analysis to provide a descriptive record of organic chemical alteration products occurring both in depth and downgradient, with additional detail in the aerobic-anaerobic transition zone that occurs near the water table. Water samples from the site of an abandoned wood-preserving plant at Jackson, Tennessee, were analyzed by high performance liquid chromatography. This was done for demonstration purposes as a field screening procedure and the data are being used to plan a more detailed sampling program at this site later this year.

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TITLE: Geochemical Reactions Between Water and Mineral Substrates (WR 88-196)

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PROBLEM: Water quality and pollution contamination depend strongly on geochemical processes involving reactions with mineral surfaces and substrates. Such processes include weathering reactions that contribute dissolved chemicals, sorption that removes aqueous species, and electron transfer mechanisms that establish redox conditions. Although extensive research has been conducted on the aqueous chemistry, minimal information exists on the corresponding solid phases and their effects on chemical transport.

OBJECTIVE: Investigate the composition and structure of common mineral surfaces and determine the extent of heterogeneity between specific surfaces and the bulk mineral phase. Determine the mechanism and rates of chemical and electron transfer between mineral substrates and surface and ground water systems. Determine the nature and extent of temporal changes in surface compositions during natural weathering and contaminant introduction and assess the effects on sorption and retardation. Assess environmental hazards due to the weathering of toxic materials contained in natural minerals and rocks and plan mitigation and cleanup under geologic constraints. Assess the effects of hydrologic parameters on rates of chemical weathering in soil profiles and watersheds and predict impacts of climate change.

APPROACH: Methods used will define concurrent changes in mineral substrates and water during geochemical reactions in natural and contaminated aqueous systems. Characterization of surface chemistry will utilize recent advances in ultra-high vacuum systems including x-ray photoelectron spectroscopy, auger electron spectroscopy, and secondary ion mass spectroscopy. Use also will be made of high-sensitivity solid state electrochemistry. Investigations will include both controlled laboratory studies and natural systems. Detailed field projects will be conducted to quantify the significance of mineral substrates in controlling major element chemistry, pH, and Eh, and as sources of trace toxic components such as chromium, copper, selenium and arsenic. Results will permit development of coupled models describing reaction kinetics and mass transport between aqueous and solid phases.

GROUND-WATER CHEMISTRY

PROGRESS: (1) Work was initiated on watershed studies in the Luquillo Rain Forest in Puerto Rico; Panola, Georgia; Sleepers River, Vermont; and the Northern Lakes, Wisconsin. These sites were selected to assess water, energy, and biogeochemical budgets associated with global climate change. Instrumented nests of tensiometer, suction water samplers, and gas samplers were installed at the Luquillo and Panola sites and water, soil, and gas samples have been successfully collected since the being of 1992. Data indicate significant variations in chemistry of the soils in the watersheds due to degree of chemical weathering, unsaturated zone hydrology, and extent of precipitation. Weathering of the granitic saprolite is almost complete to depths in excess of 10 m at Luquillo, indicating that weathering occurs at the bedrock surface at considerable depth. Above this narrow zone, soil water chemistry reflects principally atmospheric input. Relatively high nitrate levels in the soil sequence reflect microbial input and a lack of any nitrate limitation in plant uptake.

Work continued in studying rates of chemical weathering in the Merced soil chronosequence in California. Three years of chemical and hydrologic data have been collected to date, including significant changes in climatic conditions associated with the recent draught years. Rates of chemical weathering in the granitic soils, based both on changes in soil composition over 3,000 Ka in addition to current chemical flux rates, indicate that rates of chemical weathering are between 3 and 4 orders of magnitude slower than predicted based on experimental and theoretical predictions. Surface spectroscopy indicates the general lack inhibiting surface coatings, suggesting that dissolution is controlled by near-saturation thermodynamic conditions due to high silica contents and low fluid flux rates.

A study was undertaken and recently completed which evaluated the environmental impact of the Oakland Hills Fire Storm in the San Francisco Bay area on urban watersheds. The initiation of seasonal precipitation on the recently burned area resulted in a fish kill in a lake in the adjourning regional park, leading to concern that pollution resulting from the destruction of 3,000 residential structures could lead to significant environmental impacts. Water and soil samples collected from tributaries in the burn area were collected during the next 6 months, in collaboration with the regional park system to assess effects on the watershed. Results indicated that fish loss was associated with anoxic conditions produced by reaction of the ash transported to the lake. High concentrations of dissolved organic carbon, nitrate, phosphate and potassium were also contributed from the fire and subsequent hydroseeding of the burn area to prevent erosion. High lead levels were detected in the sediments due possibly to fire related effects such as combustion of lead based paints.

Lithogenic isotopes continued to be investigated by solid source mass spectroscopy. Sr and Li isotope data was collected for all five Water, Energy and Biogeochemical Balance (WEBB) sites and are proving useful tracers of source rock geochemistry and degrees of waters of soils. Strong correlations are observed in the soil chronosequence between the radiogenic signature of the isotopes and the changes in mineralogy with time. Sr, Pb, and Li isotopes were also employed as hydrologic tracers in evaluating geothermal resources and environmental impacts at Yellowstone National Park, in the Coastal Aquifer in South Carolina, sea water salinity problems in southern California, and feed lot pollution studies in Arizona. The spectrometers was updated this year with an ion counter which extends it's capability to run uranium and thorium isotopes for age dating minerals and water.

Due to the let up of the California draught, sampling of runoff and suspended sediment proceeded as part of the selenium sources project in the Central Valley. Samplers were installed that collected runoff and suspended sediment at discrete intervals as water rises in creeks following precipitation events. Analyses of collected data will test theory that selenium substituted for sulfate in soluble sodium and magnesium minerals brought to the surface by evaporation during the dry season is remobilized in the initial runoff during the wet season. Reconnaissance of the Tulare Lake Bed in the southern San Joaquin Valley is being conducted with the district office for sources of selenium related to deformed bird populations.

Work progressed on application and development of surface analytical techniques to study water-rock interactions. This work is being done in collaboration with the Center of Materials Research at Stanford University. X-ray photoelectron spectrocopy studies have been conducted on a number of issues including oxidation mechanisms associated iron oxides, dissolution kinetics of carbonate solid solutions, and weathering of aluminosilicates. Significant work was been conducted on the application scanning tunneling and atomic force microscopy in characterizing mineral surfaces. Specific applications include characterization of structure of clay minerals and determination of mineral roughness and surface morphology during reaction and weathering.

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GROUND-WATER HYDROLOGY

TITLE: The Role of Lakes in the Hydrologic System, with Emphasis on Their Relation to Ground Water (CR 74-090)

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PROBLEM: Many hydrological and geochemical processes associated with lakes and wetlands are poorly understood. Characteristics of wind and vapor profiles over lakes, which are basic controls on evaporation, have been studied in detail for only a few large reservoirs in the western United States. Many commonly used methods of estimating surface runoff to lakes and wetlands are inaccurate. Hydrogeologic controls on seepage to and from all surface-water bodies have not been studied adequately, either from theoretical or field perspectives. Research on these components of lake and wetland hydrology is especially critical to individuals responsible for management, protection, and restoration of these resources.

OBJECTIVE: Gain understanding of the basic principles controlling the interaction of lakes and wetlands with ground water, including associated chemical fluxes. Emphasize integration of theoretical and experimental field work. Emphasize the study of ground water, but include state-of-the-art studies of the atmospheric and surface-water components of lake and wetland hydrology as needed for the evaluation of the ground-water component. Evaluate error in hydrologic methodology for the various aspects of water balances of lakes and wetlands.

APPROACH: Construct theoretical and field-related mathematical models of steady-state and transient, variably-saturated ground-water conditions as related to lakes and wetlands. Choose field experimental sites in selected parts of the United States for calibration and modification of models, instruments, and methods. Measure all components of the hydrologic system, as related to the experimental lakes and wetlands, by various methods in support of the ground-water studies. Use multiple-level sensors on the lake for evaporation research. Integrate chemical flux and biological studies with the hydrologic work at selected sites.

PROGRESS: A major drilling program was completed at the Interdisciplinary Research Initiative (IRI) site in Minnesota. Four test holes were drilled to depths as great as 500 feet and additional deep piezometers were drilled in a nested pattern at each of the four sites, which permitted definition of the large-scale hydrogeologic framework at the IRI site. Data from instrumented strings of water table wells in North Dakota indicated highly dynamic changes in the configuration of the water table related to focused recharge and evapotranspiration, which resulted in change of flow direction between ground water and wetlands on an hourly to weekly time scale. Large differences in water table fluctuations were observed in different wetland vegetation zones in Nebraska, indicating the potential to determine evapotranspiration for different wetland vegetation types. Two reports were completed on evaporation at Williams Lake, Minnesota. One report was completed on northern wetland hydrology.

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TITLE: Borehole Geophysics as Applied to Geohydrology (CR 64–140)

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PROBLEM: A large amount of geophysical data is recorded for water wells and test holes, but interpretation is subject to significant uncertainties. The data are used in ground-water models to evaluate potential waste-disposal sites and the effects of ground-water contamination and to guide development of aquifers, including geothermal reservoirs. The development of quantitative log-interpretation techniques to derive more accurate data and to evaluate the statistical uncertainty in the data will reduce costs in ground-water investigations.

OBJECTIVE: (1) Evaluate presently available logging equipment and log-interpretation techniques, and develop improved instrumentation and analytical techniques for specific ground-water problems, such as site selection and monitoring for disposal of radioactive, municipal, and industrial wastes; (2) improve log-derived data, such as porosity values; (3) attempt to relate the log character of fractures to their hydraulic conductivities and to refine computer techniques for plotting hydraulic-conductivity profiles from logs; (4) develop the capability of making quantitative interpretation of borehole gamma spectra; and (5) do a statistical analysis of the magnitude and sources of errors in log-derived data.

APPROACH: Log selected drill holes, recording data in both analog and digital form, and comparing logs with results of core analyses, hydraulic-test data, and geophysical measurements made in calibration pits and blocks. Develop computer models to predict the behavior of gamma photons, electrical signals of various frequencies, and acoustic wave energy in borehole environments. Compare field-log data, theoretical predictions and hydraulic tests, core analyses, and test-pit values. Modify equipment and develop log corrections on the basis of these comparisons and calculate the statistical accuracy of log data.

PROGRESS: An experimental procedure was developed for normalizing borehole flow logs obtained during aquifer tests to remove the effects of the transient evolution of the flow field, and expanded to include the recording of transient flows at specific depths where such information may be critical in defining fracture connections between boreholes. Field tests were performed at sites in New Hampshire and Ontario, and preliminary results of the analysis published by F.L. Paillet as two symposia proceedings papers. F.L. Paillet also published a comprehensive review paper on the application of acoustic logging in geotechnical studies in The Log Analyst. R.H. Morin published four papers in scientific journals and proceedings volumes describing the field application of flowmeter/ injection method for permeability profiling in situ. A.E. Hess published a report on the plans and specifications for the recently developed heat pulse flowmeter. Two case histories of fracture interpretation from well logs and integration with other hydraulic and surface soundings were published by F.L. Paillet in conjunction with other government agencies.

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GROUND-WATER HYDROLOGY

TITLE: Mathematical Simulation of Subsurface-Water Flow Using Uncertain and Incomplete Data (CR 76-191)

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PROBLEM: Satisfactory formulations and solutions of equations approximately describing (1) movement of fluids and components contained in fluids through consolidated and unconsolidated rocks and (2) interactions of the fluids and rocks accompanying fluid movement are needed for proper understanding and management of ground-water resources. Such formulations and solutions of equations are not generally available for application to general field situations where the flow system is complex and hydrologic data are inexact.

OBJECTIVE: (1) Reformulate, as necessary, the equations describing the flow of fluids through porous or fractured rock to include stochastic processes, emphasizing equations that are suitable for field use; (2) derive techniques to solve for dependent variables and estimate parameters in the equations; (3) assess the degree of reliability and significance of the model formed by the basic equations and the parameters estimated for it in terms of the input data; and (4) assess the degree of reliability and predictive capability of the model.

APPROACH: Develop fundamental equations from methods of mathematical physics, stochastic processes, statistics, and basic physical concepts from geology, geochemistry, geophysics, and so forth. Develop solutions to the equations analytically or numerically, depending on the problem. Analyze error propagation, stability, and convergence by means of techniques of linear and nonlinear algebra if feasible and appropriate. Use techniques of nonlinear regression to estimate parameters so that the reliability and significance of estimated parameters and the predictive capability of the model can be assessed.

PROGRESS: (1) A parameter estimation package that is to be used with a modified version of the computer model, MODFLOW (MODFLOWP) was completed, and documentation for both the package and MODFLOWP was approved by the Director and printed. The documentation was used in classes taught at the Colorado School of Mines, University of Wisconsin, and the

University of Arizona. The program was successfully applied in USGS District projects in New York and Maryland. (2) The two initial papers on methods for calculating simultaneous prior and posterior (Bayes) confidence intervals for output from ground-water flow models have been accepted, pending minor revision, for publication in Water Resources Research. Revision has been completed. (3) A paper describing a method of incorporating an unknown range of possible model errors into the method of obtaining simultaneous posterior (Bayes) confidence intervals for output from ground-water flow models is through colleague review and is being revised for submission for approval. (4) The methods for calculating the posterior confidence intervals were extended to apply approximately for individual and finite numbers of simultaneous confidence and prediction intervals. A comprehensive numerical study showed that the accuracy of the approximations is quite high. (5) The report on the theory of the Modular Finite-Element Model (MODFE) was approved and is in press as a Techniques of Water Resources Investigations report. (6) A new nonlinear least squares algorithm was developed and compared with the method previously used. The new method is more efficient and robust than the old method. Aspects of the method were reported in a paper given at the conference "Computational Methods in Water Resources" held in Denver, June 9–12, 1992. A proceedings paper was published. (7) A study that considers the impact of inconsistencies between assumed and actual statistics of errors in transient hydraulic head observations used to estimate model parameters was continued. Talks on the work were give at Notre Dame, University of Virginia, and at a professional meeting. Work is continuing, and a paper is being prepared for colleague review. (8) A synthetic ground-water test case developed by Dave Pollock of Reston, Virginia, is being calibrated using nonlinear regression. This test case has been used to develop additional software that allows realistic spatial variations in, for example, hydraulic conductivity, to be represented when estimating parameters using nonlinear regression.

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TITLE: Field Applications of Unsaturated Zone Flow Theory (CR 69-200)

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PROBLEM: Various processes within the unsaturated zone affect ground-water availability and potability, as well as concentrations of water vapor and trace gases in the atmosphere. The rate at which precipitation or applied irrigation water infiltrates, its redistribution following infiltration, and the partitioning of the redistributed soil moisture between ground-water recharge and evapotranspiration affect the rate at which the ground-water reservoir is replenished and the degree to which ground water might be contaminated by chemical applications, spills, or disposal. Consequently, knowledge of and methods to quantitatively measure and predict these processes are needed to determine the impact of such societal practices as irrigation development for agriculture, the use of agricultural chemicals, and the disposal of radioactive and/or hazardous waste in the unsaturated zone on both the availability and potability of ground water. Processes governing transport in the unsaturated zone gas phase are also important in determining the potential for ground-water contamination by volatile compounds, the rate at which water is returned from soil moisture to the atmosphere as vapor, and the fate of other "greenhouse gases," such as carbon dioxide, methane, and chlorofluorocarbons (CFCs). An understanding and quantification of these processes is needed both to assess the hazards of ground-water pollution and to better predict the impact of global change on future climate.

OBJECTIVE: The goals of this project are to develop an improved understanding of the processes governing the movement of liquids and gases in the unsaturated zone, and to develop methods to quantitatively assess and model the phenomena. Processes and phenomena under investigation include those involving the movement of water and chemicals through the unsaturated zone, with particular emphasis on processes that might result in rapid transport of dissolved chemicals to the water table and (or) volatile compounds to the atmosphere. An understanding of the role of various gas-phase transport processes, on soil moisture on the distribution of volatile compounds within the unsaturated zone, and on atmospheric-unsaturated zone exchange is also sought. Processes involving plant-soil-atmosphere interactions, including evapotranspiration, plant CO_2 uptake, and root respiration of CO_2, are being studied to develop measurement and modeling techniques for those phenomena.

APPROACH: Field and laboratory investigations of the movement of water and gas and liquid tracers through both highly structured and unstructured soils are underway. Models are being developed to provide predictive capabilities for assessing the impact of agricultural and waste disposal practices on the potential for ground-water contamination. Gas phase movement is being studied through measurement of flow in open boreholes and models are being developed to simulate the observed phenomena and to assess the importance of various gas-phase transport mechanisms under natural conditions. Evapotranspiration and plant-soil-atmosphere interactions are being investigated by the development of various techniques for measuring the interchange of water vapor and other gases between the atmosphere and the plant-soil continuum. These methods include the use of chambers (flux boxes), profile or gradient methods, and eddy correlation techniques. Various modeling techniques are under development to extend such measurement in space and time.

PROGRESS: (1) An elaborate field experiment and companion laboratory experiments were set up to investigate preferential flow and transport through a highly structured clay soil at a Management System Evaluation Area (MESA) site in Missouri. Work includes investigation of gas tracers, dyes, atrazine, and conservative liquid tracers as indicators of preferential flow under various moisture conditions and, for the liquid phase tracers, water application rates. (2) A new numerical scheme to simulate one-dimensional transport through unsaturated porous media was developed, tested, and described in both a conference proceedings and a journal article. (3) Measurements were of evaporation and evapotranspiration and of CO_2 fluxes have been made over open water at Lake Shingobee, Minnesota, over subalpine meadow in the Medicine Bow Range Wyoming, and over grassland in the Little Washita basin, Oklahoma. Techniques and instruments for measuring CO_2 were tested during these measurements. (4) A paper on modeling evapotranspiration from sparse wildland vegetation in the San Luis Valley, Colorado, has been accepted by Water Resources Research. (5) Analyses of topographically induced temperature and wind effects on gas-phase circulation through Yucca Mountain, Nevada continue. The use of infrared thermography to identify air-exhausting fractures under both natural and well-injection conditions was investigated with somewhat disappointing results.

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TITLE: Ground-Water Solute-Transport Simulation (CR 85-292)

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PROBLEM: Ground-Water solute-transport simulation modeling is an important tool that aids in the analysis of ground-water contamination problems, both actual and potential. Accidental spills, leakage, and waste disposal operations can lead to ground-water contamination. The ability to analyze and predict the movement of solutes in ground-water systems is necessary to assess the effects of a contamination situation or properly design a waste-disposal operation. Laboratory experiments are essential to understanding geochemical reactions in the field and for obtaining the necessary reaction coefficients and rate constants used in transport models. Simulation modeling also is used to compare alternative strategies for aquifer reclamation. In some cases, the transported component of interest is thermal energy. Heat transport simulation is useful in the analysis of geothermal systems, waste heat storage systems, and some deep aquifer systems.

OBJECTIVE: Develop and apply new analytical, quasi-analytical, and numerical techniques to the field of saturated ground-water solute-transport simulation modeling. Develop mathematical representations of solute-porous medium interactions and chemical reactions and develop and apply efficient algorithms for numerical calculation. Apply analytical and numerical simulation modeling to laboratory and field-scale situations, both actual and experimental. Evaluate accuracy of laboratory experiments for predicting geochemical behavior of solutes in the field.

APPROACH: Formulate transport equations for systems being studied, develop or adapt various methods for solving the equations, develop and test various algorithms for numerical computation or simulation calculations, develop methods to identify and model chemical reactions, and apply the methods to laboratory or field-scale experimental situations and actual field situations. Work closely with District, other Federal, and State research projects involved in similar studies.

PROGRESS: A journal article on a computer code for simulating multispecies solute transport in one dimension with equilibrium controlled precipitation/dissolution and oxidation/reduction reactions was published. Three-dimensional visualizations of the contamination plumes at the

Rhode Island study site were developed and a talk was presented. A 2-day conference of researchers interested in multispecies solute transport with chemical reactions was organized by this project and a geochemistry project. Extensive consultation on and further development of the computer code HST3D were done with the San Diego Office of the California District working on the Ventura Regional Aquifer System Analysis (RASA) Project. Drainage boundary conditions and fault-zone permeability sheets were added to the simulator. A new nodal renumbering scheme was developed in conjunction with a partitioned, restarted conjugate-gradient interactive equation solver. This scheme has low sensitivity of iterations to the renumbering direction. A paper was written and presented at an international conference.

A model to characterize the sorption of uranium and molybdate at the Weldon Springs Site Remedial Action Project was developed in cooperation with the Missouri District and a paper was published. A one-dimensional solute transport code with multispecies sorption reactions was obtained from outside the Survey and used to simulate reaction and transport of molybdate in column experiments, and in the large-scale natural-gradient tracer test at Cape Cod, Massachusetts. An informal report was prepared for the Air National Guard, Otis Air Force Base, Cape Cod, Massachusetts, in response to a request for information on the fate of phosphorus in a sewage plume in the ground water. Experiments were designed to evaluate the fate of selected contaminants in the Snake River Plain Aquifer beneath the Idaho National Engineering Laboratory operated for the Department of Energy.

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TITLE: Application of Stochastic Processes in Hydrogeology (CR 90–319)

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PROBLEM: Many aspects of ground-water flow and transport resist standard, deterministic modeling techniques: there exist elements which either are overly complex or which are simply unpredictable. These elements may have either a spatial character, such as heterogeneity in porous media, or a temporal character, such as recharge events to an aquifer. Provided that an adequate representation can be found, these aspects of flow and transport frequently are better modeled by taking the complex or unpredictable element to be a stochastic process. Given an adequate representation, then the following questions may be addressed: (1) What is the implication of these elements for flow and transport in porous media? (2) Given observations of the physical process (hydraulic heads, concentrations, discharges), can the stochastic element be characterized (variances, length scales)? (3) Can an adequate monitoring program be designed when the physical process incorporates complex or unpredictable elements?

OBJECTIVE: The principal objective of this research is a better understanding of flow and transport phenomena when the underlying physical process contains one or more stochastic elements. A subsidiary objective is the development of a network model to evaluate sampling schemes when the physical process contains a stochastic element. An inverse procedure whereby the statistical properties of the stochastic element can be determined from the outputs of the physical process will be a necessity if these models are to be utilized. Where practicable, investigation will include development of usable computer codes.

APPROACH: Use probability theory to investigate those elements of flow and transport in porous media which are overly complex or unpredictable. The primary tools used to date to investigate problems with complex spatial elements can be loosely lumped under perturbation techniques and Monte Carlo simulation. Problems with stochastic inputs are usually best handled with transfer-function techniques. Both of these techniques usually require that a model of the system be conceptualized such that inputs and outputs are linked; in most cases, this linkage is in the form of a stochastic partial differential equation (SPDE's). Other techniques for solving SPDE's will be investigated: these include the use of Banach spaces from functional analysis and the use of adjoined sensitivities in numerical schemes.

PROGRESS: An investigation of arrival times and breakthrough curves for transport in heterogeneous porous media, entitled, "Arrival times and temporal moments of breakthrough curves for an imperfectly stratified aquifer," was published in Water Resources Research. This research was concerned with the production of mean breakthrough curves for an instantaneous pulse input when dispersion is dominated by a spatially variable velocity field (as produced by flow through a heterogeneous hydraulic conductivity field). Expressions for the mean and variance in the arrival time of a particle, given a spatially variable velocity field, also were derived. Work has been completed on a second-order correct formulation of the spatial moments of the mean tracer cloud. This initial result is limited by the restrictive assumptions concerning the nature of the velocity field correlation structure; however, some initial results were produced for higher moments (third and fourth) which indicate that, in exceptional circumstances, the tracer cloud may never become Gaussian. A correction factor for the second central moment and macrodispersivity, which allows for the extension of these quantities to more variable media, was also obtained and investigated. This work is now being prepared for submission to Water Resources Research.

In conjunction with researchers at the University of Waterloo, a Monte Carlo simulation of plume movement through a heterogeneous porous medium also has been completed. In these simulations, it was considered that the hydraulic conductivity and retardation factor were correlated, three-dimensional random processes. These simulations largely confirm this investigator's original, first-order result for transport of a conservative tracer in heterogeneous porous media. Through the simulation of reactive tracers, the investigation included the effect of a spatially variable retardation field on transport in the subsurface. The effect of this additional source of velocity variation of a particle on dispersion was investigated, as well as an effective retardation factor for the mean tracer cloud.

Also, in conjunction with researchers at the University of Waterloo, an investigation of the effect of temporal variation in the velocity field on dispersion in the subsurface has been initiated. The thrust of this research is to investigate the effect of small-scale transients on the dispersive process when these transients are effectively ignored in the modeling process. Initial results in this respect are quite encouraging.

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TITLE: Hydrologic Behavior of Cretaceous Shales (NR 81-035)

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PROBLEM: The nature of ground-water flow in low permeability settings is understood poorly because of (1) historic inattention to nonaquifer/nonreservoir rock units, and (2) inherent difficulties, related to time and size scales, of observing the phenomena of interest. Nonetheless, low-permeability units are of great importance because they mediate aquifer/reservoir behavior, have important roles in the evolution of hydrologic systems and geologic processes over geologic time, and can confine toxic materials for long periods. Cretaceous shales in the midcontinent offer the opportunity of studying, at relatively accessible depths, thick and extensive bodies of low-permeability media.

OBJECTIVE: Develop, through theoretical studies coupled with study of the flow systems in midcontinental Cretaceous shales, a better understanding of the significant flow processes in low-permeability environments. Use this information to extract information about flow history from current conditions and to predict future flow behavior.

APPROACH: Develop or improve techniques for measuring hydraulic, mechanical/hydraulic, and osmotic properties; define existing flow systems, and develop rational theoretical tools for describing flow behavior.

PROGRESS: (1) The synthesis of results from the Pierre Shale study has been completed, written and sent out for journal review. The flow system in the shale is probably the best documented naturally transient system yet described, and the only one in a relatively homogeneous low-permeability lithology. The difficulty of detecting the transient suggests that many more such systems may exist than current data indicate. (2) An analysis in progress, but in preliminary draft form, concerns the nature and occurrence of naturally transient flow (NTF) and what it can tell us about the gross scale permeability of the crust. Estimates obtained for geologic forcing by a variety of processes shows the surprising result that all have maximum values of nearly the same magnitude (about 10 to the minus 14th inverse seconds). This means that any and all NTF indicates a fairly low maximum permeability. This may be the basis of a strategy for locating large low-permeability volumes for waste isolation. (3) A range of permeability data for argillaceous media assembled earlier is currently being examined to determine their significance for the many regional flow simulations that use estimated properties for low-permeability units. The data indicate that permeabilities can be much lower than commonly assumed. This may prompt reevaluation of some simulation results.

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TITLE: Investigations of Single and Multiphase Fluid Flow, Mass and Energy Transport, and Fluid Phase Change in the Subsurface Environment (NR 78–089)

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PROBLEM: The subsurface environment is subject to both natural and man-imposed stresses, the interaction of which determines both its preservation and its employment as a multifaceted natural resource for water supply, energy production, and subsurface storage of energy and materials. Study of subsurface problems requires synthesis of a theoretical framework of physics of single and multiphase fluid flow, mass and energy transport and fluid phase change as applied to the subsurface environment, and descriptions of subsurface behavior based on measurements in complex heterogeneous environments. Improved understanding is required to solve present subsurface problems.

OBJECTIVE: Elucidate fundamental theory describing flow and transport phenomena in complex heterogeneous geologic environments. Develop quantitative methods for analysis of systems in the subsurface environment involving single and multiphase fluid flow, mass and energy transport and fluid phase change. Apply these methods to field problems in order to illuminate hydrological relationships which are important in both the preservation and optimal employment of the subsurface.

APPROACH: Measure subsurface flow and transport in the field to develop conceptual descriptions of the system. Study system behavior using mathematical models based on either hypothetical or field problem conditions. Develop practical simulation models and analytical methods for quantitative analysis of subsurface problems as well as new measuring techniques as by-products of the investigations.

PROGRESS: Variable-density flow and solute transport simulation analysis of the transition zone in the major coastal aquifer in Oahu, Hawaii, has resulted in identification of major processes controlling regional transition zone dynamics. Field measurements in Oahu, Hawaii, to determine scale effects in hydraulic and transport behavior of structured heterogeneous aquifers are complete and isotopic and chemical analysis is underway. Evaluation of regional ground-water flow in crystalline basement rocks using data collected in Sweden is underway.

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TITLE: Digital Modeling of Transport in the Saturated Zone (NR 81–120)

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PROBLEM: Management of ground-water resources requires that the extent and rate of movement of contaminants in the saturated and unsaturated zones be understood. Contaminants have been and will continue to be both accidentally and deliberately introduced into ground-water systems. Some of these contaminants are very hazardous. Because of the immediacy of such contamination problems, understanding of the physical and chemical processes affecting their migration needs to be increased rapidly, and mathematical models derived from this understanding need to be tested and documented.

OBJECTIVE: Investigate the parameters in basic mathematical transport models developed for ground-water systems to increase understanding of the factors influencing these parameters and of the interrelation between parameters. Derive appropriate two-and three-dimensional mathematical models to describe contaminant movement in complex field situations.

APPROACH: Develop numerical models, emphasizing those ground-water systems and contaminants for which transport-models seem most critical. Evaluate the accuracy and efficiency of new and existing modeling techniques through comparisons with analytical solutions, other numerical methods, and observed data from practical field problems.

PROGRESS: Analysis of ground-water systems in Donana National Park, Spain, shows that the ground-water system is critical for maintaining the ecologically important wetlands and lakes in the park. Several lakes in the park are maintained by ground-water inflow, but also, at certain times and places, lose water by seepage to the aquifer. The solute budgets of the lakes and adjacent ground-water systems are influenced by reactions in the lake and by the exchange of water between the surface and subsurface systems. The wetlands in the park exist because a thick low-permeability confining layer underlies the land surface in a large area of the park. Computer simulations indicate that the variable salinity in the confining layer results from an unusual balance between upward advection and downward diffusion of dissolved solutes, which are concentrated near the water table by evaporation. A preliminary version of a three-dimensional method-of-characteristics model has been developed. Work continues on the development and documentation of a three-dimensional version of the method-of-characteristics solute-transport module for the McDonald-Harbaugh modular flow model.

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GROUND-WATER HYDROLOGY

TITLE: Multivariate Statistical Techniques for Assessing Regional Ground-Water Quality and Quantity (NR 84–130)

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PROBLEM: Regional assessment of the chemical character of ground water requires that unbiased estimates of the chemical species in ground water be obtained. With recent regulations regarding ground-water contamination and disposal of toxic wastes, it is necessary that the methods for assessment of man-induced versus natural chemical character are not biased by experimental design, and that estimates of chemical species present in ground water are not influenced to a large degree by temporal variation and sample collection strategies. It is a requirement as well that populations which are compared are homogeneous in terms of statistical parameters. Implementing statistical design techniques early in the water-quality assessments can lead to maximizing information while minimizing the number of samples needed.

OBJECTIVE: The ultimate objective is to apply and extend statistical design theory to better understand and define ground-water quality parameters. It is the objective also to understand the relations between chemical variables in ground-water systems and to decompose the chemical variability within the system according to contributing sources. The understanding of chemical variability within the ground-water system will provide a basis for application of methodology to other areas with similar hydrogeology.

APPROACH: In order to accomplish this objective, a comprehensive investigation will be undertaken that involves collecting a considerable amount of field data in order to test improved sampling strategies. Multivariate, bivariate, and univariate statistical theory will be applied to all ground-water data collected to improve future sampling designs for ground-water studies. Stochastic and geostatistical analysis will provide better estimates of chemical parameters, which are input to geochemical and transport models.

PROGRESS: Present work activities are related to the overall objectives of the National Water-Quality Assessment (NAWQA) Program to characterize the Nation's ground and surface waters. Water-quality data have been compiled into a dataset and summary statistics for key chemical variables have been studied. The results are presently in review. Multivariate statistical methods are being used in a variety of modes to access the chemical character of ground waters in aquifers. Cluster analysis and other multivariate methods are key methods in understanding ground-water quality in study area.

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TITLE: Transport Phenomena in Fractured Rock (NR 84–134)

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PROBLEM: There has been an increasing awareness that, in many circumstances, the theories associated with the description of hydrogeologic phenomena in granular porous media are unacceptable in the description of these same phenomena in fractured rock and geologic formations having similar characteristics. Because of the wide extent of fractured formations and their various uses, including proposed repositories for radioactive waste, a need exists to describe and better understand the physics of fluid movement, deformation, contaminant migration, and energy transport under the broad range of physical situations where fractured formations exist.

OBJECTIVE: Develop mathematical models of transport phenomena in fractured rock. Use alternative conceptualizations of the medium in the development of these models because the description of fractured rock is highly dependent on scale of observation. Investigate the relevant parameters, evaluate physical situations where each conceptualization is applicable, and study the adaptability of field measurements to these conceptualizations.

APPROACH: Consider fractured rock and similar formations as a series of discrete fractures and also in various continuum conceptualizations. Develop mathematical models of transport phenomena. Use hypothetical physical situations and later, if possible, field data and field investigations to examine the applicability of these model conceptualizations and the adaptability of field measurements to these conceptualizations.

PROGRESS: Field investigations and data collection for a multidisciplinary research effort to develop field techniques and interpretive methods of characterizing and predicting fluid movement and chemical transport in fractured rock were conducted over the past year. The multidisciplinary research effort is being conducted in cooperation with six research projects, the New Hampshire and Connecticut District Offices of the Water Resources Division, Geologic Division, and several outside research institutes. The field investigations are being conducted in the bedrock of the Mirror Lake drainage basin in the Hubbard Brook Experimental Forest in central New Hampshire. These investigations couple geologic and fracture mapping, surface-and borehole-geophysics, ground-water geochemistry, hydraulic and tracer testing, and ground-water and solute-transport modeling. In addition to the overall coordination of this multidisciplinary research effort, this project conducted hydraulic and tracer tests to identify the variability of hydraulic properties of the bedrock and to identify transport properties of the bedrock. Initial interpretations of the hydraulic conductivity data were conducted to identify the principle factors affecting the distribution of permeability in the bedrock. Rock type and fracture orientation were two factors that were considered in this preliminary interpretation of data. New equipment for conducting tracer tests in fractured rock environments was developed, tested and used in tracer tests conducted in the past year. The equipment allows for the more precise identification of the quantity of the tracer being introduced into the formation, which enhances the ability to more accurately interpret the results of the tracer test.

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TITLE: Quantitative Analysis of Heterogeneous Hydrogeologic Controls on Ground-Water Flow and Transport (NR 91-152)

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PROBLEM: Heterogeneous geologic material affects ground-water flow and transport on all scales. On the local scale, changes in hydraulic and geochemical properties can occur over distances on the order of centimeters. On the intermediate scale, the heterogeneity of intra-aquifer depositional layers in unconsolidated material and fractures in consolidated material influences the pathways of ground-water movement. On a regional scale, the heterogeneities due to extensive aquifers and confining units affect the flow system in a system-wide manner that influences both the boundaries of the system and the generalized pathways of fluid movement in the system.

An assessment of the importance of heterogeneity at all scales is required to better understand and define flow and transport in ground-water systems. In addition, the relationship of field measurements obtained in heterogeneous materials to the actual occurrence and movement of the water and chemical constituents in the system must be defined.

OBJECTIVE: The objective of this project is to quantify the effect of specific heterogeneous geologic controls on ground-water systems. Meeting the objective will entail the development of methods for incorporating the effects of heterogeneous hydrogeologic controls into simulations of ground-water systems. Ideally, the characterization and quantification of the heterogeneous earth material will incorporate basic geologic information on the deposition and history of the materials under study, as well as hydraulic and chemical information.

APPROACH: The general approach is to investigate and quantify the effect of heterogeneous geologic controls on flow and transport in a ground-water system and develop methods of incorporating them in ground-water simulations routinely. The geologic depositional environment will play an important role in defining and describing the heterogeneities to be investigated.

The general approach to investigate these hydrogeologic controls will be as follows: (a) selection of the geologic control for investigation, (b) development of hypotheses to be tested, (c) selection of one or more field sites, (d) intensive analysis of "generic" hypothetical systems (based on the hydraulic and geologic information from the field sites) to corroborate or refute the hypotheses and give insight into the appropriate field measurements to be obtained to address the hypotheses, (e) specialized data collection, (f) quantitative analysis using simulation of the field sites, and (g) use of the feedback between the results of the field investigations and the hypothetical "generic" analysis to corroborate or refute the hypotheses and give insight into mechanisms that might have been overlooked.

Information on the geologic depositional history will be used in the characterization of the media under investigation at the field sites. This qualitative characterization then will be evaluated and a quantitative characterization will be developed using stochastic and (or) deterministic methodologies, as appropriate, for both the "hypothetical" simulations and the analysis of the field sites themselves. The "generic" simulations should provide much information in the determination of important processes and the indication of which field measurements will be most appropriate to collect for the specific problem under investigation.

After the generic or "hypothetical" investigations, field data will be collected, as appropriate to define the system and geologic controls. These field data required will consist of head data, borehole geophysical logs, geologist logs, surface geophysical information, water quality information, and other ancillary data. These data are will be used to characterize in a statistical sense the geologic terrain under investigation. Then methods of analysis, usually simulation techniques (deterministic and (or) stochastic), will be developed to quantify the effect of the geologic control characterized for the geologic terrain under investigation.

PROGRESS: In the first year of this project, the analysis of heterogeneous controls on ground-water flow and transport has focused on the problem at two scales. At the well-aquifer interface scale, the effect of the heterogeneous nature of the aquifer permeability and chemical distributions in the aquifer on water samples obtained from wells was identified. Work with Jacob Gibs, New Jersey District, using a multiport sampling device provided detailed time series information on the concentration of selected organic chemicals discharging at various points along a well screen. The time series information shows that trends in the quality of water sampled from wells can exist during sampling. Numerical simulation of layered systems indicates that these trends can be the result of the mixing of waters along the screened interval, and the measured trends can provide information on the distribution of the chemical species along the screened interval of the well. Also, at the well-aquifer interface scale, the experimental design and the installation of wells for another field investigation at Cape Cod, Massachusetts, done in collaboration with Denis LeBlanc of the Massachusetts District, was begun this year. At the intermediate scale, an analysis of the effect of hydraulic conductivity heterogeneities on flow paths to wells is being finalized. Hypothetical systems are evaluated under a series of differing permeability distributions, and the variability in the recharge areas of the wells examined. The results indicate that the uncertainty due to heterogeneous hydraulic conductivity distributions can be significant and should be accounted for in any "well-head protection" efforts.

Other accomplishments this year include: development and documentation of a new axisymmetric simulation model that enables the simulation of flow to wells in heterogeneous systems; corroboration of numerical flow models through the use of environmental tracers; and, finalizing of a guide for instructors of the U.S. Geological Survey's beginning course in ground-water hydrology.

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TITLE Reaction-Transport Phenomena in Hydrogeologic Settings (NR 91–153)

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PROBLEM: Ground-water transport and geochemical reactions play a significant role in many geological processes. Such processes include diagenesis, ore deposition, petroleum migration, hydrothermal activity, and evaporite formation. These processes are important in that they produce economic mineral deposits and alter the characteristics of aquifers and reservoirs from which we obtain water supplies and mineral resources. Many of these processes have been studied in terms of the geochemical reactions or the ground-water transport involved. However, in many circumstances the reactions and transport are inseparable. Because of the complexity of coupling equations of transport and chemical reactions, very few studies have been made thus far in which geochemical reactions and ground-water transport are coupled and analyzed simultaneously.

OBJECTIVE: Objectives of this project will be to understand the interaction of ground-water transport and geochemical reactions in hydrogeologic settings, including: interactions between geochemical reactions and solute transport, interactions between geochemical reactions and heat transport, and the effects of heat and solute transport on variable-density flow and transport in natural systems. Additional objectives will be to understand the implications these in interactions have for the geologic processes being studied, and to develop more efficient methods for studying processes that involve both ground-water transport and geochemical reactions.

APPROACH: The study of ground-water transport and geochemical reactions in hydrogeologic settings will be done both through field investigations and through the development and use of numerical models. Studies will begin with specific geologic processes in mind; field investigations may then be conducted and numerical models will be developed to address the particular process of interest. Field investigations may aid in constraining the numerical models, and conversely, preliminary modeling results may suggest particular strategies for sampling in the field. It is expected that considerable interaction and collaboration will occur with geochemists on a majority of the studies undertaken.

PROGRESS: A field study at Double Lakes, Lynn County, Texas, has revealed that the source of the high dissolved solids content of the water in the Ogallala aquifer on the Southern High

Plains may be from eolian activity. Chloride concentrations obtained from the unsaturated zone around the saline lake reflect the concentrations observed in the ground water beneath the sample locations. It is hypothesized that wind is picking up salts from the dry lake bed and depositing them on the land surface around and mainly downwind of the lake, where they are being incorporated into and concentrated in the recharge. This eolian hpothesis to the origin of the dissolved-solids in the aquifer is counter to an earlier hypothesis of direct transport via ground water. Chemical analyses from pore water beneath the lake indicate that the brine in the lake sediments has been moving slowly downward from the lake over the past 100,000 years. Computer simulations have reproduced the anomalous chemical signatures in some of these waters by accounting for the expected exchange capacity of the clays present. Chemical profiles below the lake are being used to constrain the timing of the lake stages during the past 100,000 years.

REPORTS PUBLISHED 1987–1992:

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TITLE: Application of the Unsaturated Flow Theory to the Phenomena of Infiltration and Drainage (WR 63-024)

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PROBLEM: Surface-runoff and various ground-water processes often are significantly influenced by water movement in the unsaturated zone. For many situations of hydrologic interest, inadequate knowledge prevents these influences from being properly taken into account in water-resource analyses.

OBJECTIVE: Test present theories of water flow through unsaturated porous materials, with particular attention on theories of infiltration and drainage. Use these theories to develop experimental techniques that will facilitate studies of ground-water recharge, runoff generation, and other hydrologic processes involving the unsaturated zone. Study unsaturated zones in various settings, particularly settings with deep unsaturated profiles, to evaluate water-flow rates and explain these rates in terms of soil, geologic, plant, and atmospheric conditions. Use the results of such studies for the assessment of water movement and attendant solute movement towards ground and surface-water supplies.

APPROACH: Test the validity and accuracy of predictive theories of water flow through unsaturated porous media by laboratory and field-scale studies. Devise improved laboratory and field methods to measure such flows and to evaluate the flow-determining characteristics of soils and sediments. Use these methods, in conjunction with unsaturated-flow theory, for field studies of flow rates of water in unsaturated-zone settings relevant to hydrologic problems.

PROGRESS: The theory and practicality of a field method for in-situ determinations of unsaturated hydraulic conductivity were tested under controlled laboratory conditions. Standard theory predicts development of a downward-growing transmission zone of constant water content when a steady flux of water is applied to the top of a uniform, unsaturated profile. The fact that the water content and matric pressure of the transmission zone correspond in theory to an unsaturated hydraulic conductivity numerically equivalent to the applied flux suggests a potentially accurate and relatively simple way to fill a critical need for in situ conductivity measurements. In a series of 28 experiments, infiltration rates corresponding to relative hydraulic conductivities of 0.02 to 0.70 of the relevant, fully-saturated value were applied to uniform, packed columns of soils and glass beads. Practical requirements of uniform-layer thickness and of time required to establish fully developed transmission zones were determined. In most cases, a uniform layer less than 1-meter thick was sufficient for application of the method to the sandy and loamy-textured soils tested. The corresponding time requirements ranged from a few hours to several days. Results also confirmed unpublished observations by C. Ripple of deviations from theoretically expected infiltration behavior. Non-ideal, non-monotonic matric-pressure histories were observed in all tests of sufficient duration to produce well-defined transmission zones. Hypotheses involving air entrapment, structural instabilities caused by changing water contents, and possible artifacts caused by the experimental apparatus were tested as possible explanations with definite, negative results.

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TITLE: Modeling and Monitoring Heat and Fluid Flow in Geothermal Systems (WR 73-102)

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PROBLEM: Analysis of heat and fluid flow in geothermal systems is needed to adequately describe the natural state of such systems and their response to fluid production for energy development. The analysis may involve analytical or numerical solution techniques, but requires delineation of realistic conceptual models for specific geothermal systems. This, in turn, requires the collection and synthesis of geologic, geophysical, geochemical, and hydrologic data. Periodic monitoring of changes in geothermal systems, including surficial thermal manifestations, can aid in understanding the natural conditions of flow and effects caused by crustal unrest and geothermal development.

OBJECTIVE: Elucidate the processes involved in geothermal systems and their response to stresses imposed by geothermal development, earthquakes, and magmatic intrusions. Develop realistic conceptual models of specific systems. Evaluate the level of natural variability in thermal fluid discharge in hot springs and fumaroles at specific geothermal areas.

APPROACH: Collect and synthesize geologic, geophysical, geochemical, and hydrologic data, including data obtainable from drill holes, for specific geothermal systems at Long Valley caldera (California), Lassen Park (California), and elsewhere. Use this information to develop realistic conceptual models of present and past flow within these systems. Apply numerical and analytical modeling techniques to quantify fluid and heat flow within these systems. Develop hydrologic monitoring programs at Long Valley, Lassen Park, and elsewhere to delineate the natural level of variability within these systems and to detect changes induced by crustal processes and geothermal development.

PROGRESS: Geothermal investigations in Long Valley caldera included (1) collection of additional gas samples from fumaroles to define changes in helium isotopes caused by magmatic intrusion and pressure changes induced by geothermal wells, (2) preparation of journal articles on these results and on an updated model of fluid flow in the hydrothermal system, and (3) monitoring of changes in hot-spring and fumarole discharge induced by geothermal development.

GROUND-WATER HYDROLOGY

A study was completed of factors causing the decline in hot-spring activity at Steamboat Springs, Nevada. The administrative report for the Bureau of Land Management describing this study documents the evidence for impacts from geothermal well production, drought, and pumpage of shallow ground water for domestic consumption. These results will form the basis for decisions by Bureau of Land Management on mitigation measures, additional reservoir testing, continued hydrologic monitoring, and permitting additional geothermal development in the Steamboat area.

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TITLE: Technical Coordination and Support of Water Resources Division Geothermal Studies (WR 72-108)

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PROBLEM: Geothermal studies in the Water Resources Division are part of multidivisional nationwide research program of the Geological Survey, funded as a line item in the Geologic Division budget. These studies require planning, technical supervision, logistical support, and coordination between the divisions. Additional coordination is required between the Geothermal Research Program of the USGS and geothermal program activities in other agencies such as the Department of Energy.

OBJECTIVE: Provide required technical, logistical, and funding support for Water Resources Division projects funded under the Geothermal Research Program.

APPROACH: The Water Resources Division (WRD) geothermal coordinator works with the Geologic Division's geothermal coordinator and the WRD Assistant Chief for Research and Technical Coordination to establish funding levels and program goals. Water Resources Division coordinator represents the geothermal research program in developing and carrying out various interagency projects such as Environmental Impact Analyses. The coordinator also participates in interdivisional program reviews and in the preparation of reports describing the geothermal research program. Technical supervision and assistance is provided where needed.

PROGRESS: The WRD geothermal coordinator provided written information for and public testimony at Congressional and Senate hearings on legislation to ban geothermal wells outside Yellowstone National Park. The coordinator also developed statements of WRD input to the Environmental Impact Statement being prepared for geothermal development on the island of Hawaii. A draft of a document summarizing the accomplishments and future plans for the Geothermal Research Program was prepared by the coordinator and two geologic division researchers. Funding and research activities were coordinated for six WRD projects and geothermal activities within the Idaho, Nevada, and Montana districts.

GROUND-WATER HYDROLOGY

TITLE: Hydrologic Studies of Heat and Mass Transport (WR 74–121)

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PROBLEM: The presence and circulation of fluids profoundly affect volcanic processes and landforms. Eruption styles and cycles are influenced by volatiles dissolved in magma and by pressure-temperature-fluid saturation conditions in the surrounding rock. The presence of magma in turn influences ground-water pressures, temperatures, and chemistry. Advective heat and mass transport affect and locally dominate the thermal and chemical regimes of volcanos. Linkages between fluid flow and mechanical deformation are suggested by observations that subaerial volcanoes deform in response to changes in water-table elevation and that microseismicity can be related to boiling.

OBJECTIVE: The general objective is to characterize selected volcanogenic hydrothermal systems by ascertaining probable recharge and discharge areas; determining modes and quantities of recharge and discharge; interpreting geologic, geochemical, and geophysical data in terms of the size, shape, and hydraulic characteristics of hydrothermal systems; and using analytical and numerical modeling techniques to develop quantitative conceptual models. Research questions include: (1) What are the modes of heat and mass transfer from magma to the shallow subsurface? (2) What are the pressure, temperature, and fluid-saturation conditions between magma and the land surface? (3) What controls the permeability of volcanoes? How does it vary in space and time? What role do temporal variations in permeability play in the evolution of volcanogenic hydrothermal systems? (4) How well-coupled are various fluid flow, transport, and mechanical deformation processes? Do relatively simple models that simulate a subset of these processes provide useful insight into transport processes? (5) How can we evaluate hydrothermal systems in composite cones dominated near the surface by cold-water recharge?

APPROACH: (1) Collect available hydrogeologic and geophysical data from the literature and from the files of public and private agencies. (2) Where data are deficient, supplement by field inventory, measurement, and sampling. (3) Develop quantitative conceptual models. Current numerical models cannot rigorously simulate the coupled problem of heat and fluid flow, solute transport, and deformation, and may need to be improved.

PROGRESS: (1) Conceptual models of the thermal structure of the Oregon Cascade Range propose either a narrow zone of magmatic heat sources, flanked by shallow heat-flow anomalies caused by lateral ground-water flow, or a wide zone of magmatic heat sources, with negligible ground-water effects. Four new heat-flow holes were sited in areas where significant heating by regional-scale ground-water flow seems unlikely. Measured heat flow (75 ± 4 mW/m) was significantly lower than the values predicted by interpolation from existing heat-flow contour maps (95 ± 7 mW/m). The relatively low values are more readily explained in terms of the ground-water flow model.

(2) A study of the hydrology of the area bounded by the rift zones of Mauna Loa Volcano was begun. Precipitation collectors were designed for 6-month-interval bulk collection of samples for stable-isotope and chemical analysis. (The proximity to the ocean and the gaseous output of the volcanoes potentially affect precipitation chemistry). Seventy-five precipitation collectors were installed at elevations ranging from sea level to 13,400 feet on Mauna Loa Volcano. In collaboration with Jim Kauahikaua and Cathy Janik of Geologic Division, 50 spring, well, and stream samples were collected and analyzed for stable isotopes and chemistry. These sites will be collected yearly for the duration of the precipitation collection. The stable-isotope data may allow determination of sources of recharge and ground-water flow patterns for the hydrothermal system of Kilauea Volcano.

(3) In collaboration with Terry Keith of Geologic Division, made the first measurements of advective heat and mass flux from the Valley of Ten Thousand Smokes, Alaska.

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TITLE: Analytical Modeling of Flow and Transport in Aquifers and Geothermal Reservoirs (WR 75-127)

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PROBLEM: Efficient management of ground-water aquifers and geothermal reservoirs requires accurate estimates of the hydraulic properties of water-bearing formations. These are needed to predict water-level changes, aquifer storage capacity, and the rate of movement of chemical species or thermal energy. Analytical models, properly applied, can often be used to estimate the hydraulic and transport properties of complex aquifer systems.

OBJECTIVE: Obtain analytical solutions to specific problems of flow and transport in water-bearing formations that can be used for evaluating the hydraulic and transport properties of aquifers and geothermal reservoirs.

APPROACH: Controlling equations for flow and transport in porous and fractured-rock aquifers are modified, linearized and solved with appropriate boundary conditions. For complex systems, the approach often involves the use of integral transforms and special methods of numerical inversion. Field data are used for case studies.

PROGRESS: Analytical (mathematical) models for the transport of heat and chemicals in porous and fractured ground-water aquifers were developed. The models involve time varying advective and dispersive transport in steady-state flow systems that may be radially diverging, converging, or planar. They were designed to account for the diffusion of heat and chemicals in a rock matrix composed of: (1) blocks of rock in a fractured-rock aquifer, or (2) mineral grains in a granular aquifer. The analytical solutions were developed in part to test, by means of field and laboratory experiments, the hypothesis that dispersion and retardation of heat and chemicals during transport is enhanced by diffusion in the rock matrix. The models are being applied to field tracer tests conducted at the Otis site, Cape Cod, Massachussetts, and to column and batch experiments conducted in U.S. Geological Survey laboratories in Reston, Virginia, and Menlo Park, California.

Analyses of field and laboratory column experiments to date suggests that the phenomenon of diffusion in the grains does indeed occur. The phenomenon was most clearly demonstrated by the laboratory experiments. Interpretation of the field experiments was obfuscated by the presence of a sewage plume. Additional field experiments are planned that will be carried out in an area away from the plume.

Improvements have been made in a new method for evaluation of an analytical solution for flow to a partially penetrating pumping well in a water-table aquifer. The method involves numerical inversion and integration of the Laplace transform solution and is computationally faster than evaluation of the real-time solution. It also allows for direct treatment of effects of variable well-discharge.

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TITLE: Hydrologic Analysis of Petrofabrics—Sandstones (WR 76-171)

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PROBLEM: Techniques for analyzing ground-water flow and for predicting the response of ground-water systems to natural and human-induced stresses require quantitative descriptions of spatial variation in permeability. New techniques for three-dimensional simulation of ground-water flow and solute transport require detailed quantitative descriptions of dispersion characteristics and the permeability tensor that are difficult and expensive to obtain with current measurement techniques.

OBJECTIVE: (1) Determine the geologic factors affecting ground-water flow and the transport of heat and solutes in porous media; (2) develop methods for estimating the relative importance of these geologic factors in various geologic settings and under various stress conditions; and (3) develop simple and inexpensive methods for measuring the requisite geologic factors and for estimating the dispersion characteristics and permeability tensor from them.

APPROACH: Develop and test methods of field samples, because sand-body geometry and the permeability tensor within a sandbody are related to the fabric of the deposits. Use trend analysis, multivariate correlation and regression, and other statistical techniques to relate sand-body geometry and permeability tensor to petrofabric. Use sensitivity analyses, including digital simulation, to determine the degree of accuracy of permeability and dispersion measurements required for adequate analyses under various conditions of stress and in various geologic settings.

PROGRESS: For the last several years, this project's efforts have been directed toward the ongoing efforts at Yucca Mountain, Nevada, in cooperation with the Nuclear Hydrology Program. Extensive instrumentation and data-aquisition systems have been installed with the objective of economically obtaining high quality hydrologic measurements in the unsaturated zone.

GROUND-WATER HYDROLOGY

TITLE: Water Wells as Strain Meters (WR 75–176)

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PROBLEM: Water wells commonly show earth-tide fluctuations. Often, the magnitude of the tidal fluctuation in a well is 1 to 2 centimeters. This fluctuation is produced by a tidal dilatation, the sum of the normal strains, of approximately 1×10^{-8}. This indicates that the water well is as sensitive to strains of the crust as is a strain seismometer. The problem with the water well is that other factors such as changes in barometric pressure, ground-water recharge, and pumping also can cause the water level to fluctuate. Use of a well for crustal-strain measurements requires separation of the strain response (the signal) from the other effects (noise). Such separation requires careful experiments in areas where we know the crustal strain.

OBJECTIVE: Use water wells as indicators of crustal strain.

APPROACH: Enhance the network of wells for the express purpose of sensing crustal strains along the San Andreas fault near Parkfield, California, with additional wells and improved instrumentation.

PROGRESS: The Parkfield network of water wells consists of 13 wells that are continuously monitored with the data telemetered via GOES satellite to the U.S. Geological Survey offices in Menlo Park, California. In Menlo Park, the data are processed and monitored. The signal is filtered, in real time, to remove both the earth tide and the barometric effects. Removing the earth tide and barometric effects makes it possible to observe crustal volume strains of the order of parts-per-billion. During the period of operation, the co-seismic strain that accompanied the Kettleman Hills earthquake (magnitude 5.5), 35 kilometers to the northeast, was observed. This has been the only major earthquake near enough to the wells to have produced a co-seismic effect. Further analysis of the record, involving better filtering, suggests a 5-day precursor in two of the wells. The precursor has an opposite sign to the earthquake co-seismic strain. Water levels went up prior to the earthquake, indicating a compressive volume strain, and went down at the time of the earthquake, indicating a volume increase associated with the event. Although the expected Parkfield earthquake has not occurred as yet, several creep events were observed by the network during the year. One of the monitored wells at Parkfield is approximately 1.6 kilometers in depth, situated about 1 kilometer east of the San Andreas Fault. This well encountered high pore fluid pressures in the bottom of the hole; the head at the top of the well is approximately 1200 meters (122 bars) above the land surface. The well head pressure is continuously measured using two quartz oscillator, high precision pressure transducers. These transducers are sufficiently sensitive to observe earth tide signals against the background of high pressure. During the year, a high frequency, continuous loop, recording setup was installed on the deep well using one of the pressure transducers. Data from this recorder will be especially interesting in the event of a Parkfield earthquake.

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GROUND-WATER HYDROLOGY

TITLE: Ground-water Monitoring Network Design (WR 82–178)

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PROBLEM: There are a variety of ground-water resource and contamination problems that involve determining the state of ground water and detecting or predicting changes in the ground-water environment. Most approaches to ground-water monitoring network design avoid a rigorous formulation of the monitoring objectives and fail to consider the important processes controlling the movement of ground water and migration of ground-water contaminants. It is unlikely that such approaches to network design will be able to effectively and efficiently monitor the subsurface environment in the face of limited resources.

OBJECTIVE: This research aims to develop statistically sound and simulation based methods for ground-water monitoring network design. The goal is to develop techniques that unify stochastic ground-water flow and contaminant transport simulation with optimization for studying ground-water monitoring options, and to explore the capabilities and limitations of various network design methods.

APPROACH: Techniques for monitoring network design will be developed using three basic classes of tools—statistically based methods for parameter estimation, stochastic aquifer simulation techniques, and optimization methods. The general approach will be to combine the parameter estimation and stochastic simulation components with techniques from mathematics and statistics to develop statistically sound and simulation based optimal monitoring network design models amenable to a wide range of monitoring objectives.

PROGRESS: Work has proceeded on developing monitoring network design models for local-scale ground-water flow and contaminant transport simulation under uncertainty. The problem studied initially was to develop a technique for designing optimal monitoring strategies for flow and transport modeling. A network design model unifying maximum likelihood inverse theory, first-order uncertainty analysis, and integer programming has been developed and is being evaluated for a variety of monitoring objectives, including reliable model parameter estimation and reliable ground-water flow and contaminant transport simulation. A second problem studied was to simultaneously estimate model parameters and characterize contaminant sources given limited field measurements of hydraulic head and contaminant concentrations. A maximum likelihood inverse model for coupled ground-water flow and contaminant transport parameter estimation and source identification was developed and tested. It was shown that it is possible to simultaneously determine model parameters and identify pollutant source locations and histories. The results from this work will be published in Journal of Hydrology.

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TITLE: Nonisothermal Multiphase Flow (WR 82-179)

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PROBLEM: Understanding multiphase fluid flow in the subsurface is of increasing importance. Large volumes of organic liquids that are not miscible with water (such as gasoline) are being introduced into ground-water systems from leaking storage tanks. Such fluids have become a major source of ground-water contamination. Understanding how immiscible fluids move in the ground, and how they interact with the sediment, the soil gas, and the ground water, is vital to protecting the nation's water supply. Information on 3-phase flow is available in the petroleum engineering literature, but much of this work is not applicable because capillary pressure effects, which are important in small-scale, near-surface ground-water systems, have generally been ignored.

OBJECTIVE: The objective of the project is to determine the adequacy of the present limited description of the mechanisms of multiphase and immiscible flow in porous media, and to develop more general and realistic fluid-flow models that will be useful in analyzing real field situations. Carry out a program of experimentation designed to test theories of multiphase flow in porous media. Develop methodologies required to measure relevant parameters both at the laboratory scale and the field scale. Develop quantitative descriptions of the flow phenomena in terms of differential equations, and seek solutions by analytical and numerical means.

APPROACH: The basic approach is to use results of computer-modeling studies and field observations to identify important problems for study. Hypotheses are developed from the existing mathematical models of multiphase flow, and experiments are designed to test the hypotheses. Tests are then run in the laboratory where all the important variables can be controlled or measured. If the tests are inconsistent with theory, new theoretical descriptions are developed. Measurements of liquid saturations and fluid pressures involve methods developed by soil physicists and petroleum engineers. Limited field experiments are performed in order to test the applicability of methodology developed in theoretical and laboratory studies.

PROGRESS: W.N. Herkelrath, in collaboration with H.I. Essaid, carried out laboratory and field investigations of multiphase, immiscible flow of fluids in sediments. As part of an effort to gain insight into the processes controlling the movement of immiscible contaminants in the field, we continued development of methods for determining the spatial distribution of water, air, and immiscible fluid saturation within a polluted ground-water system. The method involves obtaining undisturbed sediment cores from the field with fluids intact, and then analyzing the core in the laboratory to determine fluid saturations. We tested our methods at the site of a large oil spill near Bemidji, Minnesota. A new sediment sampler that improves core recovery, reduces core disruption, and minimizes fluid movement within the core was designed and tested. Tests of the new core barrel sampler run at Bemidji were encouraging; however, changes in the design were indicated and implemented. The core barrel was used in an ongoing program of field sampling at Bemidji that is yielding a three-dimensional grid of oil, air and water saturation measurements within the oil-spill zone. The saturation data were used to test a cross-sectional, multiphase numerical flow model. Fair agreement between the model predictions and the field results was achieved when representations of observed spatial variability were incorporated into the model. We also carried out laboratory investigations of fluid movement caused by the introduction of immiscible hydrocarbon liquid into uncontaminated, unsaturated, water-wet sediments. We found that adding a small amount of hydrocarbon to a sediment sample caused a large shift in the water/air capillary pressure curve. In a closed system with a constant average water content, the water pressure increased. In an open system with a fixed water pressure boundary, drainage of water occurred. These effects may have resulted from a decrease in the water/air surface tension caused by hydrocarbon film spreading and dissolution. The complexity of the response indicates that quantitative modeling of the transition from two-phase to three-phase conditions in porous media may be subject to unanticipated difficulties.

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TITLE: Theories of Water Flow and of Solute Transport in the Unsaturated Zone (WR 82-180)

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PROBLEM: The unsaturated zone has a significant influence on the quantity and quality of water resources. Current theoretical methods of evaluating and predicting this influence for a particular set of field conditions cannot adequately account for the complexity of the processes involved and for interactions among them. It is necessary to improve the current theoretical approaches to water-flow and solute-transport problems of unsaturated-zone hydrology to achieve such an accounting.

OBJECTIVE: Determine which conditions are or are not essential to realistically refining the commonly used mathematical models for unsaturated flow. Combine water-flow and water-mixing models with models for chemical reactions and biological processes by use of submodels that are rigorous and appropriate to analyses of solute transport in the unsaturated zone. Explore situations of hydrologic interest and those that may be valuable in connection with model validation or parameter determination for both water-flow and solute-transport processes. Test experimentally the theoretical conclusions reached in cooperation with other projects.

APPROACH: Consider model refinements for unsaturated flow that would account for effects of parameter hysteresis, air trapping, pore-geometry transformations and medium heterogeneity. Determine the conditions under which such refinements are essential. Develop computer-aided theoretical analyses of the interactions between unsaturated-zone waters and ground or surface waters. Attempt to integrate, for solute transport, the hydrodynamic-dispersion approach to transport with the chemist's or ecologist's approaches to chemical equilibria, chemical kinetics, and population ecology. Modify the above standard approaches to treat realistically the special conditions characterizing natural unsaturated zones, such as the presence of two fluid phases, changes in water content, wide range of soil-water fluxes, and chemical heterogeneity of the porous medium. Use or adapt existing mathematical methods, especially numerical methods and develop new mathematical methods if necessary.

PROGRESS: Completed and published a study which extended the Feed Forward (FF) method's applicability to equilibrium-controlled networks with large (more than three participants), classical-reaction-segments. Completed and published a study utilizing a new vector-spaces-based approach to solute-transport simulation. This approach permits some transport-influencing reactions of a system to be equilibrium controlled and some to be kinetics controlled. Further generalized the FF-method and continued to develop and to test a broadly applicable solute transport code that utilizes these generalizations. The improvements make it possible for the FF-method to handle networks of any size and shape, with any one or all of the reaction classes, with three participant reaction-segments of any stoichiometry and also with simple four-and five-participant segments. Participation in relatively simple reaction-segments of not only binary but also ternary compounds is made possible. Concentration-dependence of activity coefficients is taken into account. More efficient numerical methods (finite elements and certain newer methods of solving nonlinear algebraic equations) are incorporated into the code. A conclusion from this study's broad survey of FF-method's applicability is that cycles of reacting, binary solids may be an important factor that brings about insolvability of postulated, open or closed, chemical equilibrium systems. An inquiry as to how general is this result is now on the way. This result also demonstrates that (and helps to explain why) inapplicability of the phase rule always implies insolvability and impossibility to reach equilibrium, but applicability of the phase rule does not necessary predict solvability.

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TITLE: Hydrology of Fractured Rocks (WR 83–184)

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PROBLEM: Fractures often serve as major conduits for movement of water and dissolved chemicals through hard rocks in the underground. Understanding fluid flow and mass transport in fractured rocks is essential for assessing the ground-water resources of hard-rock aquifers, investigating the suitability of underground sites for hazardous waste disposal, and predicting the movement of hazardous chemicals if contamination occurs. Existing theory of fluid flow through porous media is of limited usefulness when applied to fractured rocks. The low permeability and highly heterogeneous nature of fractured rocks require extension of current theory and field methods. It is particularly important that theoretical developments be applicable on a scale commensurate with field measurements.

OBJECTIVE: (1) Develop theoretical model of fluid flow and solute transport in fractured rocks with particular emphasis on characterizing the effects of heterogeneities on different scales. (2) Develop field methods (hydraulic and tracer tests) to characterize the flow and transport properties of fractured rocks. (3) Combine the use of geological, geophysical, and geochemical methods with hydraulic and tracer tests to develop an integrated approach to modeling flow and transport in fractured rocks.

APPROACH: (1) Compare different approaches (equivalent porous media, discrete fracture, stochastic continuum) to modeling flow and transport in fractured rocks by analytical methods and computer simulation. (2) Construct mathematical model of hydraulic and tracer tests in heterogeneous fractured rocks, and apply parameter-estimation techniques to analyze test results with emphasis on detecting heterogeneous features such as a highly-permeable fracture zone. (3) Establish a field site for testing theoretical and method developments, for cooperative work with other research project with expertise in geological, geophysical and geochemical studies, and to synthesize knowledge obtained from different studies through modeling flow and transport at the field site.

PROGRESS: (1) Field work continues at the research site at the Mirror Lake drainage basin near West Thornton, New Hampshsire. Field activities during the summer and fall of 1991 include well drilling, packer tests and water sample collection at various depths in bedrock wells, seismic tomographic survey, cross-hole hydraulic tests, tracer tests, and monitoring of water level fluctuations. Preliminary analysis of hydraulic and tracer tests indicates that the water-conductive fractures identified by hydraulic tests are consistent with those identified by tomography. The fractures appear to be connected in clusters separated from one another by lower permeability rocks. (2) Research is continuing on using computer simulation to analyze ground-water movement in the Mirror Lake drainage basin and environs. A three-dimensional numerical model has been constructed with fine discretization to accurately simulate streams and topography. Results to date show the importance of stream profile in controlling ground-water flow and discharge to Mirror Lake. (3) Improved finite-difference methods were developed for modeling ground-water flow in aquifers having heterogeneous hydraulic conductivity that varies continuously. These methods were incorporated in subroutine to be used with the U.S. Geological Survey modular finite-difference model (MODFLOW). (4) A new MODFLOW module known as the Horizontal Flow Barrier Package has been documented. The module simulates the effects of thin, vertical, low-permeability, geologic features (such as a fault) that impedes the horizontal flow of ground water. The documentation has undergone colleague review and is awaiting approval. (5) A method has been developed for analyzing steady-state well test in an aquifer that contains a zone of contrasting permeability (for example, a fracture zone with significantly higher permeability than the surrounding rock). The method uses the boundary integral element method to solve the flow problem, and a nonlinear regression method to estimate the hydraulic properties, shape, and location of the zone. This work resulted in a Masters thesis.

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TITLE: Temperature Effects in the Unsaturated Zone (WR 87–193)

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PROBLEM: Transport in the unsaturated zone is strongly dependent upon temperature. However, there is a lack of quantitative information concerning the influence of temperature upon water retention characteristics, unsaturated hydraulic conductivity values, and water fluxes in natural porous materials. When compared to experimental results, existing theories underestimate the magnitude of temperature-induced changes in many pore-water and interfacial properties. Consequently, models incorporating the effects of temperature upon water retention and transport in the unsaturated zone are inadequate.

OBJECTIVE: (1) Measure the influence of temperature upon water retention characteristics, unsaturated hydraulic conductivity, and coefficients derived from these primary parameters, such as water diffusivities and capacities; (2) ascertain whether the behavior of water in close proximity to mineral surfaces is altered sufficiently to result in modified temperature coefficients for gas solubilities, adsorption, viscosity, interfacial surface tensions and contact angles, and other properties important to transport in porous materials; and (3) examine the influence of temperature on primary hydrologic processes in the unsaturated zone, such as infiltration, moisture redistribution, evaporation, and drainage.

APPROACH: Perform laboratory experiments on field cores and repacked samples to measure the temperature dependence of water-retention characteristics and unsaturated hydraulic conductivities in natural porous materials. Examine relations between matric potential, volumetric water content, and temperature in these materials by use of experimental equipment and procedures that have been modified for high temperature. Perform field experiments to determine the influence of temperature on water retention and transport.

PROGRESS: A paper was published based on a 4-year laboratory experiment concerning isothermal versus isobaric water retention in natural porous materials. The results demonstrated that the chronological order in which isothermal and isobaric desorption paths occur does not alter the final volumetric water content of a given material. This is extremely important for accurate modeling of unsaturated zone processes under conditions where both temperature and matric potential vary. Experiments were performed to examine water retention characteristics for representative elemental volumes comprised of multitextural subelements. Simple theory would predict that if the specific water capacity of each subelement is known, then the specific water capacity for the entire representative elemental volume can be predicted by a simple fraction summation procedure. However, results also indicated that if the residual saturation of one element is reached before another element has reached equilibrium, the simple theory over estimates changes in water retention. In addition, a paper was completed concerning rate-dependent hysteresis in water retention characteristics. This work confirmed that the rate of approach to equilibrium may effect the final moisture for a given matric potential. Cooperative field work was initiated to study the influence of temperature on stream/ground-water interaction, with emphasis on the effects of unsaturated zone processes on this interaction.

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TITLE: Physical Characteristics that Determine Flow in the Unsaturated Zone (WR 89–198)

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PROBLEM: Flow in the unsaturated zone profoundly influences the degradation of water quality as well as the loss and replenishment of available water resources. Unsaturated-zone physical characteristics, such as hydraulic conductivity and water retention, are essential to the determination of water and solute fluxes into ground water and to the understanding of surface-subsurface interactions. The theory describing these unsaturated-zone influences has not been adequately tested and may, in fact, be invalid for certain important cases. Limitations of present laboratory and field techniques are a major hindrance to large-scale hydrological application of unsaturated-flow theory because critical physical characteristics cannot be measured with the required speed and accuracy.

OBJECTIVE: (1) Test the validity of existing theories related to unsaturated-zone fluxes and correct or extend them, where necessary, to develop fast, accurate, practical methods for measuring unsaturated-zone fluxes and the physical characteristics that determine them; (2) apply and promote routine use of these experimental and theoretical methods in hydrological studies where the unsaturated zone plays an important role; (3) assess the importance of complicating influences (temperature gradients, dispersion, hysteresis, and so forth.) on water and solute fluxes.

APPROACH: By inventing new devices, applying newly discovered principles, and adapting technology from related and unrelated fields, develop techniques for measuring unsaturated-zone fluxes and the porous-media characteristics essential to their understanding. Integrate field, theoretical, and laboratory methods into a practical system for solving a variety of specific hydrological problems. Apply this system both to water-resource issues and to fundamental problems of unsaturated flow. Use newly developed experimental methods, alone or in combination with others, to test theory. Where necessary or desirable, derive new theory from basic physical principles.

PROGRESS: (1) The applicability of the steady-state centrifuge method (SSCM) for measuring unsaturated hydraulic conductivity (K) was extended to a wider variety of media, especially fine-textured and surface soils, by means of a newly developed modification that reduces the compressive force exerted on the sample by about a factor of ten. (2) The new version of the SSCM, applied to samples from a site in southeastern Washington, produced preliminary measurements interpretable as recharge rates. The results are consistent with known characteristics of the site and also with other recharge rate estimates. (3) We developed procedures that permitted the collection of minimally disturbed core samples in dry soils with poor cohesion, using a hydraulically driven thin-walled sampler in a carefully prewetted auger hole. (4) We applied this sampling method to obtain good quality samples from the vicinity of a hazardous waste site at the Idaho National Engineering Laboratory (INEL). Initial measurements show a distinct difference in the shape of moisture retention curves between samples from undisturbed and simulated landfill areas. Essentially identical particle-size distributions suggest that the measured difference results from structural effects. (5) We have developed an automated submersible pressure outflow cell (SPOC) system for improved speed and quality of soil moisture retention measurements. (6) We have formulated and have begun testing several alternative formulas for representing soil moisture retention with good accuracy at low as well as high water content.

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TITLE: The Fate and Transport of Immiscible Contaminants in the Subsurface (WR 89-199)

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PROBLEM: Many highly toxic contaminants commonly found in the subsurface occur as slightly soluble and highly volatile fluids that are immiscible with water. Despite their low solubility, these compounds pose a widespread potential threat to ground-water resources. Such fluids include synthetic organic compounds such as trichloroethylene (TCE) and related chlorinated hydrocarbons, polychlorinated biphenyls, coal tar and creosote wastes, and natural and refined hydrocarbons. Because of the limited knowledge concerning the multiphase nature of transport of such contaminants in the subsurface, the development of methodologies for predicting and controlling the movement and removal of such plumes is still in its infancy.

OBJECTIVE: Understand the migration and fate of immiscible contaminants in the subsurface, including the physics of multiphase flow (that is, the governing equations, the relative permeability and saturation functions, and the effects of hysteresis and porous media heterogeneity); the nature of interphase transfer processes and chemical reactions affecting transport rates and (or) physical-media properties; and the nature of biological processes in the subsurface leading to biodegradation of organic contaminants.

APPROACH: Undertake the study of multiphase contaminant problems through the development of efficient numerical models applicable at laboratory and field scale, in conjunction with experimental and field investigations. Develop methods for incorporating porous-media heterogeneity, mass transfer, and biological processes into numerical simulators. Use these models, ultimately, to simulate and predict the migration of slightly soluble, highly volatile immiscible contaminants in the field.

PROGRESS: Subsurface oil, water, and air saturation distributions were determined using 146 samples collected from seven boreholes along a 120-meter transect at a crude-oil spill site near Bemidji, Minnesota. The field data, collected ten years after the spill, show a clearly defined oil body that has an oil saturation distribution that appears to be influenced by sediment heterogeneities and water-table fluctuations. The center of the oil body has depressed the water-saturated zone boundary and the oil appears to have migrated laterally within the capillary fringe. A description of the field sampling method and the laboratory analysis technique, and a presentation of the field data from one transect, have been published in an article in the Journal of Contaminant Hydrology. A three-phase cross-sectional flow model has been developed and is being used to simulate the movement of oil and water at the spill site. Comparisons between observed and simulated oil saturation distributions serve as an indicator of the appropriateness of using such models to predict the actual spread of light nonaqueous phase liquids at spill sites. Initial results of this effort have been published in the proceedings of the U.S. Geological Survey Toxic Substances Hydrology Program Meeting (1991) and in the proceedings of the International Hydrology and Water Resources Symposium (Perth, Australia, 1991).

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GROUND-WATER HYDROLOGY

SURFACE-WATER CHEMISTRY

TITLE: Origin, Characterization, and Quantification of Natural Organic Solutes in Water (CR 68–046)

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PROBLEM: More than 90 percent of the organic solutes in water are of natural origin. These substances are known to complex trace metals, to transport pesticides, to be precursors of carcinogenic compounds upon chlorination, and to be a food source for aquatic organisms; yet, little is known about the chemistry or source of these organic materials.

OBJECTIVE: (1) Identify and quantify organic solutes that affect water-quality processes; (2) measure the amount of different organic solutes in various hydrologic environments; (3) determine the origin, structure, and reactivity of aquatic humic substances; (4) predict the processes that affect the fate and movement of organic solutes in surface and subsurface environments; and (5) determine the effects of natural organic solutes in water purification (reverse osmosis, chlorination, activated charcoal, and ozonation).

APPROACH: Conduct intensive sampling of several rivers, lakes, and interstitial waters in the United States and other countries to determine climatic, geologic, and season variations in natural organic substances. Groundwaters from different types of geologic formations will be sampled to determine possible organic variations with aquifer type. Organic substances from brackish and ocean water will be sampled for type and composition, variations from freshwaters, and for possible effects upon CO_2 and climatic fluctuations. Cooperate with other researchers and District programs with emphasis on organic contaminant movement in ground water. From the characterization of natural organic matter, correlate and predict the amount and variety of chlorinated compounds in water.

PROGRESS: Two reports were published last year and several others are in preparation. A major activity last year was the study of a watershed, Lake Skjervattern in Norway. divided into a control (no acid added) and an acidified side. Organic solutes were isolated from the control and acidified side after one year of treatment. The organic solutes have begun to change dramatically in amount and composition. Humic substances have decreased up to 5 percent in carbon and increased almost two-fold in nitrogen content. The hydrophobic/hydrophilic ratio has changed from 67:23 to 54:46 upon acidification. Spin-counting studies were conducted on ten samples to quantify the carbon seen in each sample by changed from 67:23 to 54:46 upon acidification. Spin-counting studies were conducted on ten samples to quantify the carbon seen in each sample by solid-state ^{13}C-Nuclear Magnetic Resonance (NMR) Spectroscopy. Indications are that 60 to 90 percent of the carbon is seen in the ^{13}C-NMR spectra. Studies on the organic composition of interstitial waters from Minnesota and Alaska are continuing. Results indicated that the Dissolved Organic Carbon (DOC) composition of soil interstitial waters are very different from traditional soil alkaline extracts.

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TITLE: Behavior of Natural Polyelectrolytes in Water (CR 68-132)

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PROBLEM: Natural organic polyelectrolytes are highly active materials that are present in practically all natural water systems. They interact with organic and inorganic pollutants and nutrients, influencing—and in many instances, controlling—the toxicity, rate of movement, persistence, and rate of degradation of the pollutants and nutrients in aquatic environments. Detailed knowledge of the chemistry of natural organic polyelectrolytes is therefore of primary importance in understanding the chemical changes that affect all of the components of natural water systems. Organic polyelectrolytes are partially eliminated from drinking water by coagulation and chlorination; however, the products of chlorination are not known. Natural and synthetic organic compounds are present in all natural waters. Some of these compounds are toxic or mutagenic and it is therefore important that they be identified and quantified in surface and ground water and in precipitation.

OBJECTIVE: (1) Isolation of the various organic polyelectrolytes present in natural water systems from different environments; (2) determination of the physical and chemical properties of the most abundant organic polyelectrolytes; (3) elucidation of the mechanisms of interaction of pollutants with natural organic polyelectrolytes; (4) determination of the types of chemical compounds that result from the chlorination of natural polyelectrolytes; (5) development of nuclear magnetic resonance (NMR) spectroscopic methods from the characterization of humic substances; (6) determination and characterization of selected organic pollutants in ground water; (7) elucidation of the mechanisms of humification in natural systems; (8) identification of diagnostic NMR bands of different functional groups found in natural organic polyelectrolytes; (9) characterization of the nitrogen containing species in natural organic polyelectrolytes; (10) identification of the carbohydrates in humic substances.

APPROACH: (1) Isolate chemically unique polyelectrolyte fractions using column chromatography, electrophoresis, and other techniques; (2) determine the physical and chemical properties of the fractions using small angle X-ray scattering, ultracentrifugation, and atomic, molecular, and magnetic resonance spectroscopy; (3) use carefully characterized organic polyelectrolyte fractions in experiments designed to elucidate the sorption and solubilization reactions of pollutants and nutrients with natural organic polyelectrolytes; (4) characterize the effect of fulvic and humic acids on the activity of Na ions in solution by ^{23}Na NMR spectroscopy; (5) isolate selected organic pollutants from ground waters; (6) measure the ^{15}N NMR spectra of humic substances reacted with selected ^{15}N labelled reagents; (7) measure the ^{14}N and ^{15}N NMR spectra of humic isolates; (8) isolate and identify carbohydrates from soil and compost extracts; (9) characterize by ^{13}C NMR spectroscopy humic substances isolated from water treatment plants and composts.

PROGRESS: (1) The collaborative study of compost leachate from a municipal leaf composting operation near Hartford, Connecticut, is continuing. Gravity lysimeters have been installed beneath two windows and leachate samples have been collected from the lysimeters. ^{13}C nuclear magnetic resonance (NMR) spectra of the dissolved organic carbon in the leachate samples have been measured. (2) A new model system has been developed for studying the interaction of dissolved humic substances with mineral surfaces. This system consisted of an aluminum coated glass microscope slide. The surface of the aluminum coating is covered with aluminum oxide which has a mineralogical composition similar to that of the hydrous aluminum oxide found in soils and sediments. In order to model the reactions that take place in a natural water system, these slides may be immersed in compost leachates or soil pore-waters. With this model system it should be possible to monitor the build-up of natural organic coatings on the mineral surface and to measure the thickness of these coatings. Preliminary studies have shown that it is possible to measure the thickness of the organic coating that forms on the mineral surface by ellipsometry and to measure the fluorescent spectrum of the coating. (3) A report has been completed on evidence for the downward displacement of soil pore water by chlorinated solvents at the Picatinny Arsenal, New Jersey, toxic waste study site. (4) The 5th year of field work at Lake Frywell in the Dry Valleys of Antarctica has been completed. Organic acids isolated from the inflow streams, the moat surrounding the lake, and from the water column of the lake have been characterized. ^{14}C ages have been obtained on samples from selected depths within the lake. Analysis of the diffusion profile in the lake using both inorganic and organic data has begun. A Ph.D. thesis and a journal article were published on these results. (5) The factors controlling the quantity and quality of dissolved organic carbon (DOC) in Williams and Shingobee Lakes (Integrated Research Initiative sites) in Minnesota are being studied. Summer samples of the nonvolatile organic acids from each lake and from the inflow stream at Shingobee Lake were isolated. Intensive DOC sampling combined with ultraviolet absorption measurements are being used to determine the effect of DOC on light attenuation in the lakes. (6) A study of the nature and significance of chloride interference on DOC analyses by the persulfate oxidation method has been completed. A report on the results of this study has been prepared and submitted to Environmental Science and Technology. (7) Development of a method for the isolation of hydrophilic organic acids from water has been completed. Results of the work have been accepted for publication in Organic Geochemistry. (8) The first phase of the collaborative research project with Eric Weber of the U.S. Environmental Protection Agency (EPA)

Environmental Research Laboratory in Athens, Georgia, has been completed. The project, entitled "Study of the covalent binding of aromatic amines to humic substances soils, and sediments by ^{15}N NMR," was funded from the EPA 2-percent set aside competition. This work defined the reaction mechanisms through which aromatic amines, toxic breakdown products of many important pesticides and dyes, irreversibly bind to humic substances. The first set of journal articles on this work is in preparation. Funding has been renewed for another year to extend the work to include studies on how phenoloxidase enzymes catalyze the oxidative coupling of aromatic amines to humic substances. (9) A joint research proposal with Mike Mikita of California State University at Bakersfield and Eric Weber of EPA was submitted to the U.S. Department of Agriculture CSRS Competitive Grants Program. The proposal entitled "Interactions of anthropogenic nitrogen compounds with soil organic matter," was recommended for funding. This proposal will allow us to study the mechanisms through which atrazine and its degradation products form "bound residues" with soil organic matter. The work will focus on soils from USGS Management System Evaluation (MSEA) sites in Minnesota and Iowa. (10) The first phases of studies on ammonia and nitrite fixation by humic substances have been completed. The first journal article on ammonia fixation has been published. The first journal article on nitrite fixation is in preparation. (11) Time course studies, using ^{27}Al NMR, on the disappearance of the "Al_{13}" species in hydrolyzed aluminum solutions, have been completed. This work was done in collaboration with Dave Vivit and John Hem. Studies are continuing to better define the disappearance kinetics.

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SURFACE-WATER CHEMISTRY

TITLE: Geochemical Kinetics Studies of Silicate Rock Hydrologic Systems (CR 75–189)

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PROBLEM: Adequate description of mass transport in hydrologic systems requires knowledge of the rates of the reactions among the gaseous, solid, and liquid phases present. This knowledge of reaction rates is necessary because many chemical reactions occur simultaneously in natural systems, and only a few of these appear to reach equilibrium, even after long contact times. Therefore, a complete description of the chemical processes and their rates will allow realistic modeling of mass transport in natural and perturbed hydrologic systems.

OBJECTIVE: Determine the relative importance of the factors controlling water quality and devise experiments to quantify the process by studying two model systems representing single lithologies—extrusive volcanic and shale. Determine the kinetics and mechanism(s) of these processes and the effects of natural variation on the controlling factors. Suggest reaction models by combining solution chemistry and the results of surface-alteration studies.

APPROACH: Monitor water quality from selected sources in the model study areas on a monthly basis. Monitor measurements of precipitation amounts and quality, soil temperature and moisture profiles, gravitational pore-water quality and amount, and soil-pore carbon dioxide on either a continuous or periodic basis. On the basis of these measurements, (1) describe the relations between variations in input (recharge) and output (discharge) water quality; (2) design controlled laboratory experiments; and (3) use the results of these laboratory experiments to provide data for elucidation of kinetic mechanisms. Determine changes that occur in the solid phase by use of instrumental (nondestructive) and chemical-analytical techniques.

PROGRESS: (1) Significant progress was made on the computer code describing the progress by which snow, intercepted on evergreens in mountain watersheds, becomes isotopically heavier in ^{2}H and ^{18}O. Model runs using typical winter climatic conditions predict changes that have been observed in throughfall samples. A paper describing the results is complete. The impact of the above on understanding hydrologic processes is expected to include the following: (a) How much is the groundwater-isotope value modified from the precipitation value by evaporation of snow, either while intercepted or as snowpack? How is the modification affected by climate change or vegetative cover? (b) How might glacier ice be isotopically modified during formation and what are the implications for paleoclimatic inference from glacier ice isotope measurements?

(2) Dry-deposition studies in the American monsoonal region of southern Arizona have made progress. Micro-meteorological flux measurements should begin in Fiscal Year 1992, as 95 percent of the hardware has been purchased and calibrated, the meteorological tower has been installed and cooperation from the National Park Service has been obtained. This study is a multidisciplinary study involving universities and other Federal agencies in addition to USGS. The objectives include: (a) determination of dry flux inputs that are of geologic/hydrologic interest, specifically Ca and Cl; (b) study the hydrologic cycle in an American monsoonal climate; (c) observe fluxes of water, water isotopes, solutes under American monsoonal climate; and (d) assess the impact of these processes on paleoclimatic interpretations of soil-chemical profiles and soil-development processes.

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SURFACE-WATER CHEMISTRY

TITLE: Water Chemistry of Sediment Surface Coatings (CR 76–199)

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PROBLEM: Local chemical composition of natural waters is heavily influenced by sediment surface reactions. This is attributed to sorption phenomena on the sediment surface as the sediments will carry larger concentrations of many materials such as trace metals, pesticides, salts and the like, than does the water. These sorbed species are interactive across the solid-liquid interface and may move in either direction in response to changes in chemical potential set up on either side of the interface. As is well known, sediments act as sources, sinks and carriers of a variety of chemical species. To understand the processes controlling a main source of materials that enter and exit water systems, one must understand the variety of reactions taking place that govern the distribution of chemical species between the solid and liquid phases. The solid phase acquires coatings as a consequence of its prior reactive history; these coatings are important parameters in determining the current surface chemical reactivity. An understanding of the coating process, the chemical composition of the coating (adsorbate) and the chemical reactivity of the coatings when exposed to various bulk water compositions is a prerequisite for definition, prediction and control of water quality.

OBJECTIVE: (1) Examine natural sediment surfaces to elucidate their surface chemical composition so that the rate-determining sorption processes that occur on these surfaces are described for various particle coatings; (2) correlate these sorption reactions with specific molecular species that reside on the surface; (3) examine the chemical processes by which sediment coatings are formed and the nature of the bonding between coatings and sediment surfaces; (4) determine the role that photolysis plays in substrate-coating interactions, specifically redox potential, mineral dissolution and decomposition; and (5) to determine the applicability of natural fluorescence emanating from surface coatings and materials in water monitoring movement in the hydrologic system, and identifying the materials being transported.

APPROACH: Spectroscopic methods will be used to determine the surface chemical composition of natural and prepared sediment coatings. Several techniques will be used including Fourier

Transform Infrared Spectroscopy, Fluorescence Depolarization Spectroscopy and Ultraviolet Visible absorption spectroscopy. The substrates selected for this work will be iron-oxyhydroxides, preferably Goethire, Manganite and Gibbsite. The redox reactions that are induced by changes in chemical potential or photolysis in the substrate and the coating will be examined. This data should provide fundamental information on the basic chemical and geochemical processes in water, aid in conducting evaluations of water quality, and aid in obtaining a better understanding of the reactions of the chemicals that are suspended or dissolved in water. Molecular properties of ubiquitous materials in water such as the humic and fulvic species will be determined as a step towards understanding the molecular reactivity of these materials and their role in aquatic chemistry. Steady state and dynamic depolarization studies will be carried out to measure size, shape, and molecular bonding energies of selected materials. Further characterization by three dimensional fluorescence spectroscopy of various species will be performed. Iron-oxyhydroxides adsorbates of soluble organic materials, such as acids, aldehydes, ketones, and other synthetic and natural products that enter water systems, will be photolysed to determine the interfacial effect between the adsorbate and the aqueous phase and also the adsorbate and the substrate in abiotic reactions such as photolysis. Excitation Emission Matrix (EEM) specture will be measured on samples from selected sites to determine the applicability of this measurement to hydrologic studies of material transport.

PROGRESS: Samples taken during the past 2 years, both in the summer and winter, in the Sacramento River Delta showed a wide variability in abiotic degradation. Depending on location, the values ranged from 10^{-18} to 10^{-14} in steady state hydroxyl radical concentration. Correlations indicate a relation between the photolytic activity found in parts of the river and transport of the materials that enter the river via tributaries, channels, and a network of sloughs. The present data are being used to describe the photolytic activity in the main channel of the Sacramento River from the Colusa drain to Isleton. The photolytic activity controlled by materials that enter through sloughs and timed releases are yet to be considered.

Samples taken in Yellowstone Park, Wyoming, of the tributaries to the Gibbon and Firehole Rivers which flow into the Madison River and of the Madison River itself revealed that relatively little organic matter is found in the pools and rivers which are above 30 degrees Centigrade. It was found that some anthropogenic material is injected into the Gibbon River at Elk Park and the Excitation Emission Matrix (EEM) fluorescence signature is detectable until the River enters the Madison River. Continued use of EEM spectroscopy to trace surface and ground-water transport of fluorophoric materials has allowed low cost, rapid measurement of organic fluorophores in these river systems.

A continuing surveillance of the effects caused by loss of vegetation in the Yellowstone fire, shows little changes in the photolytic index, measured as sunlight induced steady state hydroxyl radical concentration. The replacement of vegetation is not sufficiently rapid to change the sunlight intensities in the main surface water systems in the park.

Continuing co-operative studies between the U.S. Geological Survey and the Bureau of Reclamation on desalinization of water were vigorously pursued. The Yuma water desalinization plant, operated by the U.S. Bureau of Reclamation, uses reverse osmosis membranes to desalinate water. The practicality of desalinization of water depends upon the lifetime of the reverse osmosis membranes that are responsible for separating the salt from the water. The factors which degrade these membranes while in use is a prime consideration in prolonging the lifetime of the membranes and thus reducing the cost of desalting the water. Studies, by Raman Spectroscopy, on the Reverse Osmosis membranes used in the Yuma pilot plant for water desalinizating, were undertaken to evaluate the molecular degradation that occurs to the cellulose acetate membranes during plant operation. Comparison of new membranes to spent membranes showed a loss of acetate moieties in spent membranes. A controlled study of the degradating effects of pH and hypochlorite, are being evaluated. Preliminary results indicate a strong susceptibility of the membranes to hydrolysis at high pH. With chlorine present, the degradation is more rapid. The ether linkage in the cellulose ring structure is broken and the monomer linkages in the polymer are broken. A rate of acetate loss can be established which seems to correlate with loss of reverse osmosis function. Initial data indicate that, when subject to decomposing chemicals, the membrane retains its character for a given threshold time then degrades at rates dependent upon the concentration of the attacking chemicals.

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TITLE: Arid Regions Climate and Chemistry (CR 82–207)

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PROBLEM: Few guidelines have been established for the quantitative characterization of past climates in terms of proxy-climate data obtained from paleo-lacustrine systems. The connection between astronomical forcing of climate and change in the energetics of hydrologic systems has yet to be established. In particular, the application of stable isotopes to an understanding of the timing and magnitude of past changes in the Great Basin terrestrial hydrologic cycle is in its infancy.

OBJECTIVE: Determine: (1) the frequency and magnitude of change in the hydrologic cycle of the Great Basin, (2) the type and magnitude of change in the synoptic climate responsible for change in the hydrologic cycle, and (3) the cause of climatic change.

APPROACH: (1) Core closed-basin lakes such as Pyramid and Walker Lakes in Nevada; (2) Analyze organic and inorganic materials (for example, oxygen-18) from lake-sediment cores in order to establish time-series proxy-records of change in lake size; (3) perform real-time studies of the behavior of oxygen-18 in the hydrologic system in order to establish the relation between oxygen-18, lake temperature, size, and climate; (4) apply oxygen-18/climate model to core data in order to establish quantitative record of climate change for the past few hundred thousand years; (5) Develop record of lake-size change based on outcrop data; and (6) compare core-based record of lake-size change with outcrop-based record of lake-size change.

PROGRESS: Stable-isotope analyses of a 75-m core from the north end of the Pyramid Lake, Nevada, indicate that between 130,000 and 20,000 years before present (yr B.P.), Pyramid Lake was often an open system that spilled to one of three adjoining basins. Erosion of the last 20,000 years of sediment indicates Pyramid Lake receded as much as 50 m in the Holocene. The real-time study of the behavior of ^{18}O and ^{2}H in the Truckee River-Pyramid Lake system is essentially complete. We have established the relationship between change in hydrologic balance of the lake and its effect on the spatial and temporal distribution of ^{18}O. The behavior of ^{18}O has been successfully simulated using a coupled lake-thermal/isotope model. We continue to monitor the behavior of ^{13}C in the surface-water system in an attempt to understand the effect of productivity and gas exchange on its fractionation. U-series and ^{14}C age determinations on carbonates from the large tufa mounds in Pyramid Lake basin indicate they were formed between 30,000 and 13,000 yr B.P. These and other lake-level data indicate that surface- and ground-water systems in northern Nevada were extremely active between 30,000 and 13,000 yr B.P. Coupling of lake and mesoscale model is complete and the coupled model is being applied to climate-change hydrology studies of the Great Lakes region and the Great Basin of the western United States. A study of the thermal structure and water balance of Yellowstone Lake has been initiated.

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TITLE: Research in Analytical Environmental Trace Element Chemistry and Its Impact on Water Quality (CR 83-282)

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PROBLEM: The determination of inorganic constituents and their impact on water quality requires an in-depth knowledge of the interactive water chemistry relationships. The ability to measure trace and ultratrace concentration levels of inorganic constituents as well as their chemical form and speciation plays a significant role on the chemical, toxicological, transport and overall environmental impact on surface- and ground-water hydrology. The development of state-of-the-art analytical chemistry technology to the solution of specific hydrologically related problems requires extensive laboratory and field research and development effort.

OBJECTIVE: (1) Investigate and develop new concepts and approaches to the identification and measurement of inorganic constituents in water and water related materials. (2) Formulate techniques for the utilization of new field and laboratory technology for the assessment of water quality. (3) Participate in multidisciplinary research programs providing expertise in the field of inorganic water chemistry.

APPROACH: (1) Study the occurrence and distribution of inorganic constituents (trace metals, molecular ionic species, organic complexes, and so forth) in hydrologic systems. (2) Study water chemical interactive relationships and assess their impact of water quality. (3) Develop field and laboratory technology for sampling and measurement of trace and ultratrace concentrations of toxic and other inorganic constituents in water and water related materials. (4) Define relative importance of various impacts on water quality in specific hydrologic environments (such as, acid rain, geochemical industrial pollution, water treatment, agrichemical, and so forth). (5) Evaluate transport phenomena of inorganic constituents in hydrologic systems.

PROGRESS: (1) Development of technology was continued for the direct measurement of ultra-trace (nanogram/liter) concentrations of constituents in hydrologic systems by inductively-coupled plasma mass spectrometry (ICPMS). Techniques and methodology were pioneered for the measurement of stable isotope ratios of selected heavy metals at trace (microgram/liter) concentration levels in natural waters for use as tracers. Instrumentation modifications were investigated to improve measurement precision, stability and sensitivity. (2) Research continues to develop the technique of sedimentation field flow fractionation coupled with ICPMS to study the geochemistry of trace elements associated with colloidal and submicrometer diameter particulate material from natural surface water systems. (3) Research was performed, including field studies, to measure the occurrence, distribution and fate of trace metals, major water chemistry and nutrients in the Mississippi River system. This include the investigation of interaction of trace metals with other water chemical parameters, with emphasis on the distribution between various size fraction of suspended material, silts, colloids, etc.). Studies were performed to representatively collect and separate statistically valid and uncontaminated samples. Field studies also were carried out to determine interactions of contaminants with each other and suspended sediment at primary mixing zones below confluences of tributaries. This research included studies of bed sediment materials and pore water samples. (4) Research studies were undertaken to develop an understanding of the geochemistry of mercury and its fate in large river systems including the Mississippi and Colorado Rivers. (5) Research was performed to measure the relationship between water chemistry constituents and the occurrence and distribution of benthic invertebrates populations in rivers and streams. Field work was performed in the Gibbon and Firehole Rivers in Yellowstone National Park, Wyoming, and rivers and streams in the Catskill Mountains, New York. (6) Studies are underway to evaluate the chemical composition of ice layers in glaciers from the Wind River Mountain range in Wyoming. These studies will assist in evaluating climatic changes and atmospheric deposition. (7) Research was initiated to study the water quality of the Colorado River system and the impacts from Glen Canyon Dam operation on the ecology and water quality of the river systems. This included the implementation of two large scale synoptic sampling experiments in November 1990 and June 1991. Results of this research will assist in developing an understanding of the occurrence, distribution, and chemistry of water quality constituents related to controlled and variable hydrologic discharge. (8) Multi-year research studies were initiated to assess the chemical and biological water quality of the surface waters in Yellowstone National Park using state-of-the-art field and laboratory techniques.

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TITLE: Aqueous Crystal Growth and Dissolution Kinetics of Earth Surface Minerals (CR 83-284)

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PROBLEM: Accelerated decay of carbonate stone monumental works and building materials is apparent in several areas of the United States. This accelerated weathering has been attributed to air pollution and (or) acid deposition; however, little fundamental understanding of processes involved or quantitative relations between important variables are available.

OBJECTIVE: Determine carbonate stone dissolution processes and rates in natural and polluted environments. Attempt to separate the effects of wet deposition from the effects of dry deposition and normal weathering processes.

APPROACH: Onsite measurements of acid rain dissolution and damage to carbonate stone will be used, with supplemental well-controlled laboratory studies and reaction modelling. Onsite studies involve collection of rainfall leachate solutions from an inert reference surface and from limestone and marble surfaces at five acid rain impacted locations: Chester, N.J.; Newcomb, N.Y.; Research Triange Park, N.C.; Steubenville, Ohio; and Washington, D.C. Air quality, meteorology, rainfall and rain-runoff quality; and changes in the chemical composition of limestone and marble will be used to develop a quantitative description of carbonate stone dissolution and damage due to acid rain and air pollution. Laboratory studies and reaction modeling will be used to identify processes involved in acid rain damage and dissolution.

PROGRESS: A quantitative field study of acid rain and sulfur dioxide dry deposition marble damage was published in the 2nd International Symposium on Conservation of Monuments in the Mediterranean Basin, held in Geneva, Switzerland, November 19-21, 1991. This publication describes dissolution of a carbonate stone surface during episodic rain rate fluctuations in individual storms. Episodes of low rain rate (less than 5 mm/hr) were coincident with decreased rainfall pH (less than 4.0) and up to a twofold increase in marble dissolution. A manuscript describing dissolution of carbonate stone in response to episodic rain rate and chemistry fluctuations during summer storms in the Adirondack Mountains, N.Y., has been submitted for Director's approval. This study reports that high rainfall runoff from marble surfaces due to cloud bursts removes calcium sulfate minerals formed during dry periods prior to storms. In addition, dissolution products, formed by chemical weathering during periods of low rain rate and decreased rainfall pH, were washed from the carbonate stone surface during periods of high rainfall rates. A paper considering ion binding by humic substances was published in the Proceedings of the International Symposium on Humic Substances in the Aquatic and Terrestrial Environment, Linkoping, Sweden, August 21-23, 1989. This publication discussed the development of a two phase Gibbs-Donnan membrane model for describing the potentiometric properties of cross-linked weak acid polyelectrolyte gels and their linear analogues. The approach is a discrete ligand model with solution chemistry effects taken into consideration. This model has been used successfully by other scientists to interpret binding by natural organic materials.

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TITLE: Comprehensive Organic Analysis of Water (CR 84-285)

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PROBLEM: A disproportionate amount of research in water chemistry has been directed towards defining trace levels of organic contaminants in water, whereas the structures and characteristics of natural organic substances, in the dissolved, suspended, and bed sediment phases, are very poorly understood. A better knowledge of the nature of natural organic substances in water is essential to the advancement of many diverse sciences, such as organic geochemistry, aquatic biology, soil science, hydrology involving contaminant transport, and even atmospheric chemistry involving carbon cycle research. The Water Resources Division is conducting significant research on the nature of humic substances in water, which comprise less than one-half of the total organic carbon in water; a comprehensive study of the entire suite of compound classes comprising natural organic substances has been lacking.

OBJECTIVE: Conduct comprehensive organic analyses of various surface-water samples where comprehensive analyses is defined as "state-of-the-art" organic analyses on as many classes (humic substances, lipids, proteins, carbohydrates, etc.) as possible within the time and resource limitations of the project. Develop chromatographic, selective extraction, and derivatization methods for organic substance characterization by infrared, nuclear magnetic resonance, and mass spectrometric methods. Define the chemical, biologic, and hydrologic processes that both produce and diagenetically alter natural organic substances in water. Conduct interdisciplinary studies with colleagues to determine significance and mechanisms of contaminant binding with natural organic substances.

APPROACH: Characterize phytoplanktonic inputs to natural organic substances in fresh water (Island Lake, Nebraska) and saline water (Big Soda Lake, Nevada); study terrestrial vegetative contributions in the Suwannee River in southern Georgia, a subtropical environment, and in the Sagavanirtok River of Alaska, an arctic environment. Determine spatial and seasonal differences of organic substances in the dissolved, suspended, and bed sediment phases in the Mississippi River, an integrating environment, to determine the nature and importance of these various organic phases with regards to contaminant interactions and transformations. Apply techniques used to characterize natural organic substances to study organic contaminant transport processes in ground water at Cape Cod, Massachusetts, and in the Mississippi River. If unknown organic contaminants are discovered during the above studies, characterize and quantitate the contaminants.

PROGRESS: The major activity for the year was to participate in an interdisciplinary study of the water quality of the Mississippi River sampled between Minneapolis-St. Paul, Minnesota, and New Orleans, Louisiana. The project concentrated on defining sewage contaminants and on the natural organic geochemistry of dissolved and particulate phases in the river that affect contaminant transport and fate. Preliminary findings, based on fecal coliform measurements and fecal sterol analyses of bed sediments, indicate severe contamination from sewage inputs in the St. Louis, Missouri region, followed by lesser inputs in the Minneapolis-St. Paul region. Sedimentation of mineral sediment inputs from the Minnesota River combined with humic substance inputs from the St. Croix River in Lake Pepin, a natural river lake on the Mississippi River, is believed to be an important mechanism for removing contaminants, such as PCB's, input from the Minneapolis-St. Paul region. An ongoing research study of organic functional groups that contribute to the strong-acid characteristics of fulvic acid from the Suwannee River, Georgia found that carboxyl groups combined with ester and ether functionalities alpha to the carboxyl group explained the strong-acid characteristics. The finding of α-ether polycarboxylic acids for this fulvic acid is especially significant because this functional-group arrangement is known to efficiently complex trace metals and calcium in water.

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SURFACE-WATER CHEMISTRY

TITLE: Solid Phase Chemistry and Related Environmental Processes (CR 89–316)

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PROBLEM: Solid phase chemistry plays a significant role in the environmental impact of inorganic constituents in natural aquatic systems. Considerable research is being performed to characterize the phenomena governing the geochemical processes effecting metal concentrations in natural waters; however, it is not sufficient to only study species concentrations in waters, sediments, and partial extracts thereof. A fundamental knowledge of the chemical reactions occur at the interface between the solid and liquid is required to understand the effect of sedimentary materials on water quality. The processes governing the partitioning of metals between the two phases, and the contribution of solid-phase coatings to the transport of metals between the two media, are little understood. To model the environmental impact of metals in natural waters, solid-phase surface analysis is needed to characterize the chemistry involved at the reactive interface between sediments and surrounding waters.

OBJECTIVE: Define the processes involved in and governing metal transport between sediments and surrounding waters. Characterize the chemistry and chemical reactions at the sediment-water interface and supporting substrates in samples from pristine and polluted environments. Define the chemical and physical changes that occur at the surface of sediments subjected to changing aqueous environments.

APPROACH: Develop techniques for the collection, preservation, and trace element characterization of sediments for species transport studies involving sediment/surface-water interaction chemistry. Special emphasis will be placed on studies of environmentally toxic elements. Surface trace-element chemistry of nonconducting materials (sediments) will be characterized via mass spectrometric measurements of laser-ionized surface sputtered neutral materials generated by ion bombardment. Develop a comprehensive, and simultaneous analytical technique for the determination of 14 environmentally toxic elements in small samples. Develop sampling and analytical technology for the study of organic arsenic species in natural waters. Major, minor, and trace element characterization of small amounts of suspended materials collected on membrane filters–with direct application to glacial dust and the Mississippi and Colorado Rivers water-quality studies. Trace element studies of high-country lake waters and sediments in small watersheds. Collaborate with Colorado District's U.S. Army Rocky Mountain Arsenal program. Review proposals submitted to the Army for pollution transport studies through ground- and surface-water systems. Participation in Colorado District pollution transport studies pertinent to contaminant aqueous/sediment sorption.

PROGRESS: Continued efforts to establish an analytical laboratory dedicated to the determination and speciation of toxic elements in waters and sediments. Research initiated evaluating solid-state detectors on a high-resolution optical emission spectrograph for trace-element analyses of solid materials, such as, suspended sediments, and glacial deposits. Sampled waters and suspended sediments from the Arkansas, Colorado (Grand Canyon), and Mississippi Rivers. Consulted for the Natural Resources Authority, Hashemite Kingdom of Jordan, on water analysis by induction-coupled argon plasma atomic emission spectrometry. Continued research activities on trace element characterization of waters and sediments from alpine lakes and small watersheds in the Rocky Mountains, and contaminant-transport studies within a shallow, confined aquifer below a toxic-waste dump site at the Rocky Mountain Arsenal. Initiated research on development of field sampling and analytical technology for characterization and speciation of mercury in waters and sediments at ultra-trace levels of concentration. Baseline studies will be performed on samples from remote alpine lakes in the Rocky Mountains of North America and the Altai Mountains of western Siberia, Russia. Subsequent sampling sites will be remote lakes and urban hydrologic systems in New England and adjacent states. Continued collaboration with the Colorado District program at the Rocky Mountain Arsenal in studies of natural and induced contaminant-transport within a confined aquifer. Initiated collaborative research with climatologists from the Russia Academy of Science in the trace element characterization of glacial deposits, firn, and alpine lakes and streams that form the headwaters of the Ob River in western Siberia, Russia.

SURFACE-WATER CHEMISTRY

TITLE: Sedimentary Geochemical Processes Affecting the Exchange of Nutrients and Transition Metals Between Sediment and Water in Riverine, Estuarine, and Lacustrine Environments (NR 76-065)

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PROBLEM: Benthic-sediment exchange processes are potentially a very significant source-sink of nutrients and metals within an aquatic system. Too often, the quantitative effects of these processes are only estimated when biogeochemical cycling and ecological responses are being considered. Understanding geochemical processes that control nutrient and transition metal chemistry of natural waters is requisite for predicting the effects that human-induced events will have upon natural geochemical cycles and for determining the use of natural waters as a resource (for example, estuarine waters as food resources).

OBJECTIVE: (1) Study the important geochemical processes affecting the nutrient and metal composition of, and exchange between, sediment and water in several different aquatic environments; (2) aid in developing methods for determining nutrient and metal fluxes between sediment and water; and (3) assess the influence of human activities on natural geochemical cycles.

APPROACH: Sample and analyze surface water, ground water, and sediment-pore water for nutrient and transition-metal content of aqueous phases and associated solid phases. Measure nutrient and metal exchange in natural and laboratory-controlled environments to determine the effects of changing environmental conditions (temperature, salinity, nature of inorganic and organic substrates, bioturbation). Analyze samples by use of colorimetry, ion chromatography, and flame and flameless atomic absorption spectrophotometry. Model results in terms of solution-mineral equilibria, ion exchange, and advective-diffusive transport through porous sedimentary media.

PROGRESS: Several long cores from Lake Oahe, South Dakota, have been analyzed for radionuclides and stable elements. These data have been used to construct a sediment transport/deposition model that characterizes nonsteady-state sedimentation in a reservoir lake. The combination of fine-scale sampling and rapid sedimentation produce radionuclide distributions that can be used to estimate the detailed chronology of particle transport processes in the Oahe Reservoir system. A largely self-consistent and generally quantitative treatment of the ^{137}Cs data suggests processes to which characteristic times may be associated. These times include (1) an integration time of several years reflecting retention of the sediment-bound tracer in regions within and external to the reservoir, and (2) a relaxation time of approximately 15 years reflecting a decreasing rate of sediment accumulation that is ascribed to shoreline stabilization. The distribution of sedimentary arsenic confirms the validity of the variable sedimentation model. In 1977 the discharge of arsenic-contaminated tailings was redirected and the unrestricted input of arsenic to Lake Oahe ceased. As a result of this remedial action, the concentration of sedimentary arsenic decreased dramatically. In the upper section of the core, above the depth represented by the year 1976, the distribution of lithologically discriminating chemical elements, calcium and vanadium, relate to major flow events in the Cheyenne River basin. Because there is minimal diagenesis of chemical constituents in these rapidly accumulating sediments, stable element signatures may be used to reconstruct hydrologic events in drainage basins that provide abundant sediment sources for lakes and reservoirs.

The geochemistry of thermal springs in Lake Baikal, Russia, has been investigated. Pore waters, extracted from sediment cores, were analyzed for their oxygen and hydrogen isotopic compositions and major ion chemistry to determine the source of water from a vent area for diffuse lake-bottom thermal springs or seeps in Frolikha Bay, northeastern Lake Baikal. The delta ^{18}O values of pore waters range from -15.2 per mil to -16.7 per mil and delta D values range for -119 per mil to -126 per mil (both isotopes determined relative to standard mean ocean water [SMOW]). Bottom water in Lake Baikal has delta ^{18}O value of -15.6 per mil and a delta D value of -120 per mil. Pore waters in the vent area are significantly enriched in Mg, K, Ca, and especially Na and have the lowest delta D and delta ^{18}O values; these pore waters are isotopically and chemically distinct from pore waters in other, more typical parts of the lake. The pore-water isotopic data fall on a local meteoric water line, and covariations in water isotopes and chemistry are not consistent with evaporation or hydrothermal water-rock interaction. The thermal springs represent discharging meteoric waters that have been gently heated during subsurface circulation and are largely unaltered isotopically. Chemical variations are most likely due to dissolution of subsurface evaporites. The transition metal geochemistry of sedimentary pore waters associated with hydrothermal activity in Lake Baikal has been studied. Chemistry of pore waters extracted from Baikal sediments that are affected by hydrothermal activity is substantially different from chemistry of pore waters extracted from normal sediments. The hydrothermal pore waters are strongly influenced by sulfur geochemistry whereby transition metals react with carbon and sulfur to produce reduced Fe and Mn carbonates and Fe, Ni, Zn sulfides. The low concentrations of transition metals in hydrothermal pore waters are in sharp contrast to much higher concentrations in normal pore waters. Although sulfate reduction occurs in normal sediments, the production of reduced species is not sufficiently developed so that this process affects the concentrations of dissolved transition metals.

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TITLE: Hydrogeochemical Controls on the Migration of Radionuclides from Uranium Mill Tailings (NR 78-092)

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PROBLEM: Uranium mill tailings and related forms of low-level radioactive waste contain elevated contents of naturally occurring radionuclides that have been brought to the surface, processed for the recovery of uranium and other components, and then disposed of in near-surface impoundments. The long-term fate of the tailings and their constituents will be determined by surficial earth processes.

OBJECTIVE: Study the chemical form in which radionuclides and selected stable elements are retained in surficial earth materials, particularly uranium mill tailings, and identify processes operating in natural aqueous and terrestrial systems that may influence the transport of these constituents from these earth materials.

APPROACH: Determine the partitioning of nuclides and elements of interest in tailings, ores, soils, rocks, and waters through the use of leaching and sorption studies, particle sizing, radon emanation measurements, and nuclear emulsion microscopy.

PROGRESS: As a spinoff of work on the microbial reduction of uranium, a soil washing procedure was developed aimed at decontaminating uranium-bearing soils and related earth materials. Samples included uranium ore and mill tailings, radium refinery soils, and soils from artillery ranges receiving depleted uranium munitions. The environmentally benign procedure developed involves extraction of uranium from the soil with sodium bicarbonate and its subsequent precipitation by means of microbial reduction.

The environmental cycling of iodine in terrestrial ecosystems has important implications in terms of plant nutrition and the fate of ^{129}I, a long-lived fission product. Anaerobic cell suspensions of *Shewanella putrefaciens* and *Desulfovibrio desulfuricans* with hydrogen as the electron donor were shown to be capable of reducing iodate (IO_3^-) to iodide (I^-). A membrane-free, soluble fraction from broken cells of *D. desulfuricans* was also capable of iodate reduction. Aerobic cell suspensions of *S. putrefaciens* failed to reduce iodate.

Experiments are underway on the microbial reduction of plutonium, and a literature review was recently completed preliminary to initiation of studies on the microbial reduction of technetium. The studies described above are being done in cooperation with projects in the ecology (Derek Lovley) and ground-water chemistry (Jess Cleveland) discipline groups.

Due to its long-half life, radiotoxicity, and role as the radiogenic parent of ^{226}Ra, the fate and transport of ^{230}Th is of interest in radioactive waste management. We have focused our work on the behavior of trace concentrations of thorium in sulfuric acid/ore component systems typical of sulfuric acid-leach uranium mills. Sorption of thorium by pre-existing crystals of quartz, jarosite, hematite, sodium feldspar, gypsum,, galena, bentonite, and fluorite was studied under conditions that simulate an acidic uranium mill effluent environment. Up to 100 percent removal of trace quantities of thorium (approximately 200 parts per billion (ppb) in 0.01 N sulfuric acid) from solution occurred within 3 hours with fluorite and within 48 hours in the case of bentonite. Quartz, jarosite, hematite and sodium feldspar, gypsum, and galena removed less than 15 percent of the thorium from solution. In coprecipitation trials, barite and gypsum were formed in the presence of thorium (approximately 1,000 ppb). Approximately 60 percent of the thorium present in solution coprecipitated with barite, while less than 5 percent of the thorium coprecipitated with gypsum under similar conditions. When jarosite was precipitated in the presence of high concentrations of thorium (approximately 0.2 M Th in 0.01 N H_2SO_4), a significant amount of thorium was incorporated in the precipitate.

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TITLE: Carbon Fluxes in Hydrologic and Geologic Processes (NR 79-099)

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PROBLEM: Carbon fluxes are an important aspect of many hydrologic and geologic processes. For example, on a global scale, rising atmospheric CO_2 concentrations and the increasing use of fossil fuels have led to concern for the future effects of atmospheric CO_2 on global climate. Anticipating the effects of atmospheric CO_2 requires an understanding of the role of natural hydrologic and geologic processes in the global carbon budget. On a more local scale, ground-water and surface-water contamination problems are often associated with locally significant changes in the transport and sedimentation of carbon. This project evaluates carbon fluxes by studying the hydrologic and geologic processes responsible for them. These studies emphasize the need to understand both human impacts and the evidence for natural changes in local to global carbon fluxes before man's influence.

OBJECTIVE: Evaluate local to global carbon fluxes associated with hydrologic and geologic processes. Determine the geochemical mass balance for carbon in selected hydrologic/geologic systems. Determine the processes most important in controlling carbon fluxes. Investigate the possibility of past variations in the world's (natural) CO_2 balance, and apply this information to the prediction of future global CO_2 fluxes. Understand the role of fluxes of carbon compounds in selected local ground water and (or) surface water contamination problems.

APPROACH: Estimates of carbon fluxes and quantities are derived from direct measurements, published literature, and computer models of hydrologic and geologic processes. Analytical methods utilized by this project include infrared gas analysis, gas chromatography, high performance liquid chromatography, and coulometric and potentiometric titration techniques. Stable isotope and ^{14}C measurements are acquired where appropriate. Available data are used to constrain computer models based on chemical thermodynamic and kinetic relationships and the conservation of mass and charge.

PROGRESS: Project activities have encompassed both field measurements and modeling. A soil CO_2 field monitoring program has been established as part of the Water, Energy, and Biogeochemical Budgets (WEBB) program at the Sleepers River Experimental Watershed in

Vermont. Gas chromatographic techniques have been implemented for analyzing carbon dioxide in 5-ml soil gas samples. An infrared photosynthesis analyzer has been adapted to measure CO_2 fluxes through soil and snow surfaces. The initial focus of these studies is to understand the processes that control CO_2 fluxes over diurnal to seasonal time scales.

Modeling studies have focused on aspects of the carbon cycle that are particularly relevant to the geochemical effects of CO_2 and to long-term geochemical predictions. To analyze the sediment record of carbon-cycle change, and to assist in long-term CO_2 predictions, modeling techniques have been developed to accommodate carbonate dissolution and other sediment interactions. These techniques have been used to document a significant correction of previous analyses of the whole-ocean carbonate-ion response to perturbations. Ocean/atmosphere/sediment modeling suggests that, if man burns all of the world's fossil fuel reserves, the average lysocline and atmospheric CO_2 concentration may remain perturbed for thousands to tens of thousands of years.

This project has also contributed substantially to Bureau and Division climate and global change program development.

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SURFACE-WATER CHEMISTRY

TITLE: Geochemical Cycling of Trace Elements and Nutrients in Natural Water Systems (NR 81-109)

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PROBLEM: Natural water systems provide a wide range of conditions within which to examine the geochemical behavior and cycling of trace elements and nutrients relative to hydrochemically important mineral reactions. Processes of mineral dissolution, alteration, and genesis exert strong controls on the concentrations of chemical species in natural water systems and thus on water quality. Chemical composition of atmospheric precipitation input to terrestrial watersheds affects mineral reaction rates and may regulate reaction pathways and products. Knowledge of the geochemical behavior and cycles of major elements, trace elements, and nutrients is essential in order to understand and predict the consequences of deliberate or accidental anthropogenic additions of these substances to the environment.

OBJECTIVE: Define the role of mineral-water interactions in determining the chemical composition of natural waters with emphasis on major elements, trace elements, and nutrients. Quantitatively describe the geochemical behavior of these species in fresh-water, estuarine, and marine environments. Assess the impacts of anthropogenic contributions on natural cycles in these systems and evaluate the hydrogeochemistry of major elements, trace elements, and nutrients as it relates to water resource utilization.

APPROACH: Geochemical mass balance studies of the flux of major elements, trace elements, and nutrients in natural water systems are developed by detailed sampling and chemical analysis of input waters and outflow waters. The critical reactions that control changes in water chemistry are identified and quantified through examination of the solids that the waters contact and react with and through laboratory studies of rock soil-water interactions.

PROGRESS: Investigations of biogeochemical processes in watersheds are being continued. Emplacement of shallow wells across the Mill Run and Shelter Run valleys in the Massanutten Mountains of Virginia has enhanced knowledge of the shallow ground-water flow systems at these localities. Detailed investigation of the clay minerals from the well cuttings is providing information on the weathering processes occurring in the watersheds. Preliminary sampling of oxygen-18, deuterium, radon, tritium, and chlorofluorocarbons in well water and several streams in the Catoctin Mountains, Maryland, is being conducted to explore the use of these dissolved species for identifying the ages, sources and flow paths of waters feeding the streams. If successful, these methods will be fully implemented and extended to other watersheds. Geochemical mass-balances have been determined for four watersheds in the Catoctin Mountains, Maryland, and two watersheds in the Massanutten Mountains, Virginia. The mass-balances are being used to infer the weathering reactions and watershed processes that control water chemistry in these systems. Preliminary examination of the data sets for watersheds in Maryland and Virginia are being made for long-term (10 years) trends in surface water chemistry. At both localities small, but statistically significant, upward trends in major cations and sulfate have been observed. This work is in progress for trends in precipitation at these sites. Work on changes in hydrogeochemistry induced by storm events is being continued in watersheds on several different bedrock types.

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SURFACE-WATER CHEMISTRY

TITLE: Distribution and Speciation of Metals in Sedimentary Environments (NR 86–135)

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PROBLEM: It is not sufficient to know only the total concentrations of metals in environmental samples. The partitioning of metals between solid and solution phases and the speciation of metals in these two phases among free ionic metal compounds and metal inorganic and organic complexes needs to be determined to develop correct models of environmental systems. Prediction of the response of aquatic and sedimentary systems to environmental changes and determination of the toxicity of metals in these systems are dependent on metal speciation. An example of an environmental problem involving organo-metal associations is the spread of toxic metals with the transport of sedimentary material. The presence of organic coatings on sedimentary matter and the large surface area per unit weight of small sediment particles result in high metal concentrations in the small-particle fraction. These small particles are more easily transported by the water column than coarser sedimentary material. This mobility means that toxic metals can extend beyond a point source. How environmental changes affect the partitioning and speciation of metals, and the rate at which these changes occur, needs to be evaluated.

OBJECTIVE: Determine inorganic-organic reactions by which toxic metals are retained in, or mobilized from, the sediment and the rates at which these processes occur.

APPROACH: Determine the distribution or partitioning of metals between solution and solid phases. Evaluate the speciation of dissolved, free, inorganic complexed metals and organic complexed metals. Measure the rate of change in species composition in response to changes in environmental conditions. Use atomic adsorption spectroscopy in the determination of total trace-metal concentrations in aqueous and sedimentary samples; use liquid chromatography in examination of the speciation of metal complexes; and use electrochemical analysis in the determination of free and labile metal ions in solution. Use these techniques not only to determine the distribution of metals between phases, but also to determine the classes of organic compounds with which the metals are associated. Study the rates of adsorption-desorption processes. Study the speciation of metals in the systems, not only by use of extraction methods or specific ion electrodes, but also by use of biochemical methods coupled with liquid chromatography and electroanalytical techniques to determine specific information about the redox chemistry, chemical associations, and bioavailability of toxic metals.

PROGRESS: The focus of this study continues to be the role of organic matter in the transport of metals in aqueous environments. There has been no way to unequivocally differentiate polar metallo-organic compounds from inorganic metal compounds in natural samples until supercritical fluids were applied to the problem by this project. The novel approach to studying the metallo-organic compounds present in natural samples that is used in our laboratory has confirmed our original hypothesis that measurable percentages of organically-bound metals are present in our samples. The use of supercritical fluids to fractionate the metal-containing organic matter from natural samples has provided insight into the mechanisms for interaction between metals and organic matter in samples where metallo-organic compounds are found. At present, our work with metallo-organics focuses on solid samples including sediment and suspended particulate material. Our project uses supercritical fluids in the speciation of metals in several Survey studies. Improved techniques for identifying organically-bound metals are being applied to suspended and bottom material from the Calcasieu River, Louisiana, a former Hazardous Substances Hydrology Program site where our project has linked the transport of metals to the presence of drift (suspended particulate material) in the water column. The question of whether metals, in particular, organically-bound metals, are diffusing from the sediment to the overlying water column is being addressed at a Natural Resources Damage Act site in Idaho. There is a state-wide concern in Florida about the presence of mercury in the Florida ecosystem food-chain. The possibility of organically-bound mercury being part of the mechanism for entry of mercury into this food-chain is being investigated. Mercury is known to be 10 to 100 times more toxic when organically-complexed than when in the inorganic state.

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TITLE: Chemistry of Hydrosolic Metals and Related Constituents of Natural Water (WR 57-076)

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PROBLEM: Hydrosolic metals are elements that form hydroxides with low aqueous solubilities. They may form colloidal suspensions (hydrosols). Some of these elements are toxic and they may interfere in various ways in practical utilization of water. Understanding the occurrence and behavior of these elements in water is complicated by effects of pH, oxidation and reduction, formation of complex ions, coprecipitation with other elements, and intricate chemical kinetic relationships. Because natural aqueous geochemical systems generally are not at equilibrium, although some are at steady states, development of models and concepts appropriate for treatment of nonequilibrium systems has been a major objective in recent project studies.

OBJECTIVE: Define dilute-solution chemistry of elements of interest in the detail that is sufficient to apply findings to natural water systems; the final reports should be useful in predicting the behavior and fate of hydrosolic metals and associated substances, either in natural or polluted systems, as guides for designing optimal data collection programs and aids in the interpretation of water analyses and related hydrologic data.

APPROACH: Develop a predictive inorganic chemical model for behavior of the element of interest in dilute solution. Models are based on chemical thermodynamic and kinetic data from literature and appropriate laboratory experiments and may postulate either equilibrium closed-system or irreversible open-system conditions. Theoretical concepts are used in these models to expand structural and electronic bonding behavior of the elements studied. Models are tested in chemical laboratory experiments and by applying them at appropriate field sites. Models are modified as necessary to allow for kinetic and biochemical factors.

PROGRESS: Interpretive report on coprecipitation experiments of Mn oxides in the presence of cadmium was published in *Geochimica et Cosmochimica Acta*, Volume 55. A theoretical model using principles of coordination chemistry was developed to explain the strong effect of Cd on rate and extent of production of Mn^{4+} in the precipitated oxides. Laboratory experiments to define chemical conditions in Pinal Creek, Arizona, surface flow and tributary ground water showed that simply raising pH, if dissolved oxygen is low, favors precipitation of manganese carbonate species such as kutnahorite as seen in subsurface crusts. Stream-bed encrustations in which manganese oxide species predominate are favored by the greater availability of oxygen from the atmosphere. A paper on this subject by Carol J. Lind and J.D. Hem has been accepted for publication in Applied Geochemistry. It correlates mineral speciation and solution chemistry data for Pinal Creek.

Preliminary results from ^{27}Al nuclear magnetic resonance (NMR) determinations by Kevin Thorn of the Organic Polyelectrolytes Project, Denver, Colorado, showed a significant proportion of Alb, polymeric aluminum hydroxide, prepared at pH 4.90 was apparently the $AlO_4Al_{12}(OH)_{24}{}^{7+}$ ("Al^{13}") complex reported by others who have used the NMR technique. The Al13 species disappeared during aging. Further work is required to define the significance of this. A paper on the subject was given by Dave Vivit at the 1992 Spring meeting of the American Chemical Society in San Francisco.

A chapter on historical trends of SO_4 and Cl concentration and yields per unit area of drainage for the St. Lawrence, Lower Mississippi, Upper Columbia, and Allegheny River basins was completed and is being processed for publication in the USGS National Water Summary volume for 1990-91. Upward trends in SO_4^{2-} yields for the St. Lawrence and Lower Mississippi appear to be explainable as a result of increases in air-borne SO_4^{2-} during the 1905-1980 period of the analytical data. Flow regulation in the Allegheny basin above Pittsburgh has substantially improved quality of low-flow water at Pittsburgh since the late 1960's.

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SURFACE-WATER CHEMISTRY

TITLE: Origin, Fate, and Transport of Organic Compounds in Surface and Ground Waters and Their Effect on Water Quality (WR 83-204)

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PROBLEM: There is a general lack of knowledge of fundamental processes governing the fate and transport of anthropogenic organic compounds in surface and ground waters. Interactions of organic contaminants with natural organic coatings on sediments and aquifer porous media are not well understood. Furthermore, abiotic and biological transformations of organic contaminants in surface and ground waters require extensive fundamental investigations if their effects on water quality are to be understood.

OBJECTIVE: (1) Determine physicochemical and biological processes, controlling the fate and transport of organic compounds in surface and ground waters. (2) Determine bioavailability of hydrophobic organic contaminants to stream biota. (3) Study transport of organic compounds from rivers through estuarine systems.

APPROACH: (1) Water, suspended sediments, biota (plant and benthic invertebrate tissues) and bed sediments, will be collected from the San Joaquin and Sacramento Rivers and Delta, and from San Francisco Bay. (2) Samples will be analyzed using electron-impact and chemical ionization ion-trap mass spectrometry. (3) Seasonal variations in organic contaminant loads, as affected by fresh-water influxes and salinity gradients, will be investigated. (4) Bioconcentration of selected hydrophobic organic contaminants will be studied.

PROGRESS: Studies of the fate and transport of pesticides in the Mississippi River and its tributaries are in progress. The entire navigable reach of the Mississippi River and all its tributaries were sampled during two cruises in 1991 and one cruise in 1992. The entire river is contaminated with a complex mixture of agrochemicals and their transformation products derived from nonpoint sources. These compounds include triazine, chloroacetanilide, thiocarbamate, phenylurea, pyridazine and organophosphorus pesticides. The Upper and Middle Mississippi River Basin farm lands are major sources of herbicides that are applied to corn, soybeans, and sorghum. Farm lands in the Lower Mississippi River Basin are a major source of rice and cotton herbicides. Input of the five major herbicides, atrazine; cyanazine; metolachlor; alachlor; and simazine, to the Mississippi River are mainly from the Minnesota, Des Moines, Missouri and Ohio Rivers. Ratio's of desethylatrazine to atrazine in the Mississippi River and its tributaries suggest that, during base-flow conditions, there is a significant ground-water contribution to the river. The Mississippi River thus serves as a drainage channel for pesticide-contaminated surface and ground water from the midwestern United States. Estimates of annual mass transport of these compounds indicated that significant amounts of pesticides are discharged into the Mississippi River Delta and Gulf of Mexico. For example, over 160 metric tons of atrazine were discharged into the Gulf of Mexico in 1991.

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SURFACE-WATER HYDROLOGY

TITLE: Precipitation-Runoff Modeling of Watershed System CR 77-228

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PROBLEM: Modeling of watershed response to normal and extreme climatic conditions or to changes in the physical conditions of a watershed requires the simulation of a variety of complex hydrologic processes and process interactions. Some of these processes are well understood at a point or for a small area; others are poorly understood at all scales. Increasing spatial and temporal variability in climate and watershed characteristics with an increase in watershed area adds significantly to the degree of difficulty in investigating and understanding these processes. Research is needed to better define these processes and to develop techniques to simulate these processes and their interactions at all watershed scales.

OBJECTIVE: Investigate watershed hydrologic processes and processes interactions to (1) improve understanding of watershed system dynamic; (2) develop computer models to simulate and evaluate the effects of various combinations of precipitation, climate, and land use on streamflow, sediment yield, and other hydrologic components; and (3) develop procedures and techniques to estimate model parameters using measurable watershed and climatic characteristics.

APPROACH: Develop, test, and verify model components of individual hydrologic processes using data from watershed studies conducted by the U.S. Geological Survey (USGS), other Federal Agencies, and universities. Model components will be coupled in a modular-design watershed modeling system that supports both operational applications and further research work. For hydrologic processes that are poorly defined or for which there is insufficient data, field studies will be conducted to investigate these processes and develop new or improved simulation capabilities.

PROGRESS: Development of the Modular Hydrologic Modeling System (MHMS) reached the beta test stage. MHMS was installed at selected U.S. Geological Survey, U.S. Forest Service, National Aeronautics and Space Administration, and university sites to begin initial system testing. The Rhea-Colorado State University (RHEA-CSU) orographic precipitation model was modified and linked with a geographic information system (GIS) to facilitate model application to a variety of spatial scales, and facilitate transport to a variety of mountain regions. Linking the RHEA-CSU model to the USGS Precipitation-Runoff Modeling System (PRMS) provided improved simulation results for a 750 km^2 test basin in the Gunnison River basin, Colorado. A grid-based characterization of this basin, using 25 km^2 grid cells, produced equivalent simulated streamflow to a characterization using 17 topographically defined subareas. A methodology was developed to use output from a mesoscale atmospheric model to compute input to the RHEA-CSU model. Evaluation of the ability of general circulation models (GCMs) to simulate daily sea-level pressures for North America indicates that GCMs simulate the spatial and temporal variability of pressure well, but have problems simulating the proper magnitudes of pressure. Examination of reservoir management practices in the Delaware River basin to minimize the effects of climate change indicate that reservoir storage is more sensitive to climate change than is the position of the salt front in the estuary under current management practices. Adverse effects of climate change on both storage and the position of the salt front can be minimized by altering management practices. Research on subglacial water-flow processes at South Cascade glacier, Washington, has provided the first field verification of a subglacial conduit and data that indicate multiple hydraulic processes contribute to water routing. A program to inventory the glaciers of the United States using a GIS was initiated. The role of a climate factor in delineating regional trends in the statistical parameters of annual flood distributions of small basins was developed using ensemble analysis. Average values of the statistical parameters show strong regional trends in log space. The effect of climate embodied in the regional trends may help in defining geographic limitations on networks designed for regional flood information.

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TITLE: Statistical Analysis of Errors in Hydrologic Models (CR 83-279)

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PROBLEM: Uncertainty in application of physically based surface-water hydrologic models is a function of adequacy of the conceptualization of the processes involved and of the quantity and quality of data available to use as input to the model. In any type of modeling exercise, even if the physical processes are well understood, spatial heterogeneities make application of the model on a basin-wide scale problematic, and it is almost always necessary to use some form of spatial averaging to obtain "effective" input variables. The over-all goal of our research is to investigate (1) model output errors as a function of model complexity and uncertainty in model input; (2) derivation of simplified yet physically based models that are appropriate to use with limited data; (3) ways of evaluating and coping with uncertainty caused by spatial variability of input variables.

OBJECTIVE: Develop unified approach to analyzing and partitioning errors in hydrologic modeling with particular attention to scale and spatial averaging problems; develop improvements to existing practices; and develop new approaches to managing error levels within the constraints of reduced budgets.

APPROACH: Use probabilistic and statistical techniques to estimate the individual contributions of various sources of error in hydrologic modeling.

PROGRESS: (1) Investigations of properties of the random topology channel network model, especially for large networks [our strategy in looking at the effect of model input error has been to randomize various components of model input, including channel segment properties, such as length, and channel segment configuration. This has been done primarily via the random topology model used by geomorphologists since the 1960's. Hence, our investigations into model input error have led to a number of related studies on the properties of this and other random network models]: (a) Continued investigations of properties of the width function; and (b) studied distribution of subnetwork magnitudes for randomly selected points in a topologically random network. (2) Investigations of spatial random network models [the random topology model does not give a unique spatial definition to networks being modeled. Hence, we have seen the need to look at random models that are well-defined spatially; we have used rectangular grids to do this]: (a) Studied application of the one-parameter Gibbsian family of distributions (well-known for applications in thermodynamics and statistical mechanics) for modeling spatial behavior of channel networks; the parameter is a measure of drainage efficiency of the network: (i) Developed Markov chain procedure for simulating networks under the Gibbsian distribution; (ii) developed parameter estimation procedures for networks defined using digital elevation data (that is, for "topographic trees"); (iii) developed regionalization methods for predicting the Gibbsian parameter as a function of map scale; (iv) looked at methods for using this model to predict network width function; and (v) Applied methods developed using digital elevation data for Willow Creek, Montana. (b) Investigated extension of Gibbsian family of distributions to a two-parameter family, and worked on inference problems for this family, including point and interval estimation using bootstrap procedures. (c) Investigated fractal properties of spatial models as measured by the behavior as the grid spacing grows smaller. (3) General extensions of previous results giving hydrologic response as a function of fundamental basin characteristics: (a) Previous results (that is, instantaneous unit hydrograph peak as a function of network magnitude) have assumed linear channel routing with a constant basin-wide velocity and no overland flow delay. Some time has been spent looking at how such results might be generalized (nonlinear routing, spatially variable velocity, and so forth). (b) Investigated optimal ways to estimate hydraulic parameters such as the effective basin-wide velocity. (4) Work with Bob Lichty on error analysis of regionalized flood magnitudes: (a) Investigated influence of climatic factors on regionalization error; (b) mapped flood distribution moments based on ensemble averaging; and (c) collaborated with Marshall Moss on accuracy of spatial precipitation estimation for climate models. (5) Work by Skip Vecchia: (a) Developed new methods for model identification analysis for periodic autoregressive moving average time-series models [these models are extremely useful for characterizing stochastic properties of seasonal time-series such as monthly streamflows]. (b) Developed a new efficient method of prediction for spatial regression models with correlated errors using maximum likelihood methods. The methods can be used for evaluating uncertainty in spatially distributed inputs to hydrologic models. (c) As part of the global change research initiative, developed a stochastic model for generation of joint-station monthly streamflows on the Upper Gunnison River Basin. The model will be used for studies on the sensitivity of the Gunnison River Basin to climatic change.

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SURFACE-WATER HYDROLOGY

TITLE: Transport and Degradation of Organic Substances in Streams (CR 77-301)

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PROBLEM: Organic substances in streams affect the quality and uses of the water. To determine the effect of organic substances on water quality, the physical, chemical, and biological processes involved in the transport and degradation of these substances must be understood. Procedures for measuring or estimating the rate coefficients describing these processes must be developed. Models incorporating these coefficients then must be developed for predicting the fate of organic substances in streams and their effects on water quality.

OBJECTIVE: (1) Study the fundamentals of volatilization, dispersion, and sorption on sediments of organic substances in water; (2) develop submodels of these processes, including methods for measuring or estimating the process rate coefficients; and (3) integrate these submodels into overall transport and fate models for organic substances in streams.

APPROACH: (1) Conduct controlled laboratory studies to determine the volatilization and sediment sorption of specific organic compounds, both as single components and as mixtures; (2) conduct controlled field studies to test, adapt, and (or) develop transport and fate models for organic substances in streams; and (3) apply the models to field problems.

PROGRESS: Project personnel participated in both the upriver and downriver phases of the June–August, 1991, September–November, 1991, and March–May, 1992, Mississippi River sampling trips. Experiments are being conducted to determine the trihalomethane and nonpurgeable total organic halide formation potentials for sample waters from 12 points along the Mississippi River between Minneapolis, Minnesota, and New Orleans, Louisiana, and also for the Missouri and Ohio Rivers. Preliminary results indicate that the formation potentials decrease with distance downstream. Also, the trihalomethane formation potential increases with pH, whereas the nonpurgeable total organic halide formation potential decreases with pH. The bromide concentration was larger in the Missouri River than in the Mississippi River upriver of their confluence. This larger bromide concentration resulted in the formation of more brominated trihalomethanes in the Missouri River sample and in the samples from the Mississippi

River below the confluence than in the samples from above the confluence. Suspended sediment, colloid, bottom sediment, and back-water samples are being prepared for analysis of selected hydrophobic organic compounds by gas chromatography/mass spectrometry. Preliminary analysis of the data indicates that the loads of industrial and agricultural chemicals on the suspended sediment are lower than in previous years.

Fish tissue and triolein-strip integrator samples also are being prepared for analysis of selected hydrophobic organic compounds by gas chromatography/mass spectrometry.

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TITLE: Paleohydrology and Climate Change (CR 90-321)

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PROBLEM: To anticipate the effects of potential climate change (natural or anthropogenic) on hydrology and to assess hydrologic trends will require an understanding of past long-term hydrologic variability. There also is a critical need for data on extreme floods for engineering hydrology and flood-hazard mitigation. Probably the best information on hydrologic variability and extreme floods is provided by paleohydrologic and other proxy data analyzed with the help of hydrologic models. Methods for extending existing climatic and hydrologic records over long-time scales are needed. A relatively new approach, one that complements hydrologic modeling efforts, involves the application of paleohydrology to determine regional scale hydrologic variability over relatively long-time intervals (100 to 10,000 years). Existing techniques for paleohydrologic reconstruction have large errors; hence, there is a critical need to improve paleohydrologic techniques.

OBJECTIVE: The primary goals of this project are to (1) improve techniques to reconstruct the fluvial history of river basins, particularly for extreme floods; (2) improve the understanding of hydrologic and hydraulic processes to improve numerical models of rivers; and (3) improve the understanding of links between climate and hydrology. These goals are closely related because the development and use of paleohydrologic techniques require an understanding of geomorphic response to climate change and an improved understanding of hydrologic and hydraulic processes.

APPROACH: Interdisciplinary, process-oriented research is used to study past and present hydrologic and climatic conditions in mountainous environments, particularly the Rocky Mountains. The research includes (1) paleohydrologic research that consists of selecting several basins in different climatic regions to construct the fluvial history of each river basin. Using different methods (such as step-backwater, critical depth, and tractive force), estimate paleoflood discharges. Using a variety of geochronologic techniques (dendrochronology, carbon-14, thermoluminescense, and other absolute- and relative-age dating techniques), improve methods to make high-resolution time sequences of alluvial stratigraphy; (2) conduct instream, laboratory and numerical modeling studies to improve hydrologic and paleohydrologic methods of estimating velocity and discharge; and (3) analyze hydrologic, paleohydrologic, and climatic data to quantify long-term variability and to improve the understanding of the links between climate, fluvial processes, and hydrology. To better understand extreme floods, mitigate flood hazards, and decrease the uncertainty of paleoflood techniques, an interdisciplinary study of floods during or immediately after floods is being made.

PROGRESS: The study of the paleoflood hydrology of Arthurs Rock Gulch, Colorado Front Range, is finished and the report is in review. The study investigates the fluvial history of the river basin, and the development and testing of methods used to conduct paleofluvial studies in mountain rivers. Additional paleohydrologic research in the Rocky Mountains has begun. This research includes studies of the Bear Creek watershed west of Denver, Colorado, and the Gunnison River Basin, Colorado, in collaboration with the Global Change Program. Hydraulic data for the North Saint Vrain Creek at the Rocky Mountain Hydrologic Research Center is being analyzed to improve methods to estimate velocity, discharge, and paleodischarge in mountain rivers. Initiated water-chemistry studies of headwater basins in the Colorado Rocky Mountains related to the National Water-Quality Assessment (NAWQA) program. Conducted interdisciplinary research of two flash floods that occurred in Colorado during 1991.

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TITLE: Numerical Simulation of Hydrodynamic Processes in Rivers, Estuaries, and Coastal Embayments (NR 69-019)

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PROBLEM: Technical solutions to the problem of investigating and managing waste movement and disposal in regulated rivers, estuaries, and embayments require qualitative and quantitative assessments of the interactions among waste constituents undergoing dynamic transport. Mathematical, numerical, computer-simulation models offer one very powerful solution. Because water is both the vehicle by which the waste constituents are transported and the media in which the constituent interactions occur, the temporal and spatial variations of the flow appreciably govern the interactions qualitatively and quantitatively. Design of the desired simulation models depends in large measure on accurate mathematical-numerical representation of the hydrodynamics of the transient-flow process.

OBJECTIVE: (1) Explore thoroughly the hydrodynamics of one-, two-, and three- space dimensional transient flows (including the transport and interaction of constituents) in water ways and waterbodies; (2) develop mathematical-numerical techniques with which to simulate these processes; and (3) provide the hydrologist with a simulation system comprised of rational mathematical-numerical models for evaluating the effect of past, present, and projected changes in prototype-waterbody systems.

APPROACH: Derive mathematical models comprised of sets of nonlinear, partial differential equations representing various transient flow conditions. Develop numerical techniques to simulate the various flow regimens represented by the models. Use field data gathered at specific field sites and (or) hypothetical data reflecting a projected change to provide the necessary boundary-condition information and driving function with which to particularize model solution. Use large-capacity, high-speed digital computers and videographic output equipment in making the simulations.

PROGRESS: (1) Continued research into means for improving numerical simulation of an integrally combined transport process in flow/transport models has resulted in two higher-order numerical schemes. Tests reveal that one of these can be pushed to 5th order accuracy with little apparent sacrifice of numerical efficiency. Both schemes are being studied with regard to their suitability for operational modeling.

(2) Implemented a full, three-dimensional, flow/transport model of Massachusetts and Cape Cod Bays with a colleague from Energy and Marine Geology, U.S. Geological Survey, Woods Hole, Massachusetts. The proper calibration of this model has underscored the importance of careful treatment of open boundary conditions at an ocean interface—in this case, the Gulf of Maine. Initial results from the model for selected conditions of tide, wind, and salinity have appeared in print.

(3) Advised and consulted with district office personnel, with personnel from other state and federal agencies, and with private engineering consultants on flow/transport modeling. In particular, the groups included district project personnel in Connecticut and New York working on an investigation of salt water intrusion in the Hudson River, South Carolina; District personnel, studying the Cooper River, New Jersey; District personnel studying several small estuaries; and Florida District personnel contemplating and planning a contaminants movement study in the St. Johns River.

(4) Organized a technical session focused on the selection and (or) development of computational grids, boundary condition data and eddy viscosity values for use in two- and three-dimensional flow/transport models. Subsequently, chaired this session at the 2nd International Conference on Estuarine and Coastal Modeling in Tampa, Florida, November 13–15, 1992.

(5) Prepared and presented an intensive, week-long, hands-on, one-dimensional flow modeling course at the Southeastern Regional Headquarters in Atlanta, Georgia, last October 21–25, 1991. This new course, prepared with another National Research Program colleague and a fourth colleague from the Office of Surface Water, offered a thorough review of the underlying physics and hydrodynamics, as well as full treatment of the mathematical representation of unsteady, open-channel flow. Implicit finite-difference numerical methods like those used in the BRANCH one-dimensional model were stressed, as were the considerations and techniques for particularizing, implementing, and calibrating a model for a specific site. Students were assigned class problems for solution using workstations.

(6) Led a workshop on utilization of Network Common Data Format (NetCDF) data and file handling in simulation models for the Office of Surface Water at their annual meeting, March 1992, held in Memphis, Tennessee.

(7) Continued research into the numerical treatment of boundary conditions used with different numerical methods and various combinations of dependent variables. This resulted in a diversity of findings for a selected set of test cases. Although preliminary findings now appear in print

(Lai and others, 1992) this investigation continues to be hydrodynamically and numerically fruitful, as well as revealing with regard to practical measures for operational modeling.

(8) Gave an oral presentation, jointly, with G.L. Granger, on the design, objectives, capabilities, and current operational status of SIEVE, a scientific, interactive, extensible, visualization environment, that provides a general-purpose, X-window-based means for viewing and appraising input/output model data on UNIX workstations. The presentation was made at the 1st NCAR Graphics Users Conference, June 17–18, 1992, National Center for Atmospheric Research, Boulder, Colorado. Also, served as an invited panelist at this conference: topic of panel discussion; "Future Needs for Scientific Data Visualization."

(9) Prepared a paper entitled, "Modeling Transport Processes in the Coastal Ocean" with Alan F. Blumberg, HydroQual, Inc., Richard P. Signell, Energy and Marine Geology, U.S. Geological Survey, Woods Hole, Massachusetts. Paper was subsequently presented, orally, by Blumberg to a meeting of the National Research Council Committee on Geophysical and Environmental Research, at Woods Hole, Massachusetts, June 1, 1992.

(10) Demonstrated the investigative capability of a two-dimensional, vertically integrated, simulation model for revealing the effects on flow, circulation and transport caused by locating highway right-of-way causeways through shallow, tidal wetlands. This effort produced several results of environmental engineering significance. A professional journal paper with two National Research Program colleagues has been prepared and submitted for peer review.

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SURFACE-WATER HYDROLOGY

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TITLE: Computational Hydraulics for Surface Water Problems (NR 79-096)

PERSONNEL: Vincent C. Lai, Project Chief
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PROBLEM: Because of the rapid increase in computer power and capacity, fast changing computing environment, and extensive involvement of the Water Resources Division (WRD) in computer modeling of various practical water problems, there is little time to carefully appraise up-to-date numerical tools and modeling techniques. Inadequate use of computational methods and numerical analyses, improper handling of parameters and data for numerical modeling, and indiscriminate application of questionable or outdated modeling techniques all lead to serious simulation errors or total information losses. In general, the progress of numerical analysis lags well behind the development of modeling methods; thus, many a new numerical model is built without commensurate numerical analysis methods to assess its numerical qualification, accuracy and reliability. Uneconomical and incomplete numerical experiments are often the only resort for model examination—a particularly acute problem for the scale and the kind of modeling work dealt in the WRD. Another important problem with computational hydraulics today is the fact that the field encompasses a much broader scope than merely delving into numerical details, which is less perceived by modelers and which must be addressed properly in computational hydraulics research.

OBJECTIVE: (1) To investigate, compare, or appraise various numerical approaches, methods, schemes, or modeling techniques for hydraulic or hydrodynamic simulation; to explore or test newly introduced numerical methods for their adequacy and applicability in hydrologic projects; or to devise or develop new numerical modeling approaches for simulating surface-water problems. (2) To conduct studies on numerical stability, convergence, accuracy, efficiency, parameter identification, sensitivity analyses and other numerical properties associated with complex, and often nonlinear, models in computational hydraulics and water resources problems. (3) As coherent manifestation and comprehensive implementation of the above study objectives, a multicomponent (for example, hydrodynamic, transport, sediment, diffusion-dispersion and other components), multidimensional (spatial and temporal) surface-water flow model using a multimode numerical method is set as its ultimate modeling goal.

APPROACH: (1) Review existing and explore newly introduced numerical approaches, methods, schemes and modeling techniques. Investigate, for given flow problems, the effect and quality of simulation results due to change in numerical schemes and methods, and for fixed schemes and methods, the same due to change in application problems. Compare relative merits of different methods and techniques from various viewpoints. (2) Review physical concepts of nonlinear effects in various flow problems, and rapidly-varied unsteady flows in particular. Study higher-order terms in partial differential equations and their effects in different numerical schemes. Investigate numerical aspects of convergence, stability, accuracy, sensitivity, etc. Derive guidelines for rational and effective modeling and simulation from these studies. (3) With the ultimate goal of a comprehensive model, set in Objective (3) in mind, merge a varied number of components for multicomponent models, use a different number of dimensions for multidimensional models, and combine various numerical methods and schemes for multimode numerical models. Gradually work toward a greater and more effectively coupled surface-water flow model.

PROGRESS: (Project Chief was on leave to teach in Taiwan University from February 1991, to February 1992.) A systematic study for generalization of multicomponent-multimode riverine and estuarine flow modeling has been carried out. A report discussing an n-component riverine flow model using the multimode method of characteristics has been drafted. This study should help to broaden the perspective of hydromechanics modelers. The research has been extended to conduct indepth analysis of the Courant number, the most important number in computational hydraulics.

A series of extension, revision and refinement tasks has been performed for unsteady (reversible) alluvial-channel (movable-bed) flow modeling. A program documentation and users' manual is now in preparation. The model includes three basic components (two hydrodynamic waves and one bed-deformation wave), accepts user-supplied sediment-concentration equations, and is capable of simulating both (and genuinely-coupling) both unsteady hydrodynamic and sediment transporting flows.

With a final objective of compiling some useful guidelines for surface-water flow-model developers and users in mind, a set of investigations into several nonhomogeneous terms, with the friction term in particular, in the governing partial differential equations was started some years ago, and a part of preliminary results was published in a few conference papers. Recently, this effort was intensified and a few full papers more complete and up-to-date than the earlier ones are under preparation.

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TITLE: Simulation Modeling of Hydrodynamic Systems (NR 80–104)

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PROBLEM: Managing water use in riverine and estuarine systems requires an understanding of the governing supply, circulation, mixing, and flushing processes. Qualitative and quantitative evaluation of the hydrodynamic and transport properties of such water bodies can be computed by means of mathematical-numerical simulation models. To accurately simulate temporal and spatial variations of flow, which significantly define the transport processes, the simulation model must be capable of accounting for hydraulic and tide-induced fluctuations, water withdrawals, discharges, winds, nonuniform geometric configurations, and other human-induced or natural factors.

OBJECTIVE: (1) Investigate and develop various mathematical-numerical techniques with which to simulate the hydrodynamics of one-, two-, and three-space dimensional transient flows in various water bodies; (2) evaluate and (or) develop methods to describe the transport of solutes in such water bodies on the basis of the comprehensive flow information derived from flow simulation models; and (3) develop and implement an operational system in support of flow/transport simulation models.

APPROACH: Use large-capacity, high-speed digital computers and various supporting peripheral equipment. Derive and develop mathematical models, constituting approximate numerical solutions to the governing nonlinear, partial differential equations to simulate the transient flow and transport processes. Use data, collected at specific locations or hypothetically imposed, to provide the required boundary-condition information with which to effect the numerical solution.

PROGRESS: Improved methods and greatly diminished initial-value data constraints for initiating numerical simulations using the branch-network model have been developed enabling cold start-up for highly complex open-channel networks. Additional enhancements and extensions of the branch-network model have been developed and a ported version for the a Unix-based distributed information system has been prepared for distribution.

Continuing research into the numerical treatment of open-boundary conditions using different numerical methods and varied combinations of dependent variables has revealed mixed behavior for particular cases—a journal paper is in process. Preliminary findings have been published (Lai and others, 1992).

Investigation of the potential of a two-dimensional vertically-integrated simulation model for analyzing the effects of highway-causeway placement on the hydrodynamics and transport in estuaries has continued and a journal paper with colleagues has been prepared for peer review.

Consulted and advised a number of District Offices on surface-water modeling projects. Included among these are projects involving investigation of saltwater intrusion in the Hudson River, water-quality conditions in the Foster Creek and Back River tributaries of Cooper River, and freshwater influence on saline conditions in Indian River Lagoon. Extended the branch-network model to allow for culvert-type hydraulic structures to assist the South Carolina District in the Foster-Creek/Cooper-River project.

Organized two technical sessions on the use of open-channel network simulation models in addressing environmental problems for the multidivisional American Society of Chemical Engineers Water Forum '92 National Conference to be held in Baltimore, Maryland, on August 2-5, 1992.

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SURFACE-WATER HYDROLOGY

TITLE: Hydrologic Regression and Data-Network Design (NR 82–125)

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PROBLEM: There is a need to develop methods by which the USGS hydrologic data-collection activities can be evaluated objectively and modified, when necessary, so that the efficiency of its operations will be maximized.

OBJECTIVE: Produce objective methods for hydrologic network design and methods for information transfer.

APPROACH: Use cross-validation and computer simulation of hydrologic processes to evaluate the statistical and economic measures of the hydrologic data-collection programs.

PROGRESS: Progress was made in four areas of investigation: (1) With personnel from the Branch of Systems Analysis, the New Jersey District, and Ohio State University, regression models were developed to predict the probability of a water quality constituent being above a specified threshold. The regression models are based on observed water quality data and GIS based land-use information. (2) A geostatistical approach to analysis of the National Trends Network (acid rain) was developed with the help of personnel from the Central Region Branch of Regional Research and the Geologic Division. This analysis was used to determine the most cost-effective network of sites to operate in the event of a budget cutback. (3) As a result of participation in a World Meteorological Organization (WMO) workshop in Koblenz, Germany, and a comparative study, the WMO recommended further development and testing of the generalized-least-squares method of network design developed on this project. The WMO feels that this technique may be a useful technique to adopt for its member countries. (4) Initial data collection and development of a basin model to study the hydrologic effects of climate change on the Appalachicola-Chattahoochee-Flint (ACF) River basin has taken place. The model developed to study the effects of possible climate change may also be useful to the National Water Quality Assessment (NAQWA) study also being carried out in this basin.

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Driver, N.W., and Tasker, G.D., 1988, Techniques for estimating storm-runoff loads, volumes and selected constituent concentrations in urban watersheds in the United States: U.S. Geological Survey Open-File Report 88–191, 80 p.

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TITLE: Regional Hydrologic Processes (NR 84-133)

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PROBLEM: The regional nature of hydrologic processes is generally defined in terms of shared meteorologic and basin characteristics. Inferences have been attempted by regressing the measures of hydrologic interest against such characteristics. Such treatment has been insufficient to fully explain the variations or extremes in discharge patterns observed within a geographic area. Long-term influences, such as decadal to centennial climatic fluctuations, need to be considered, and the stochastic structure of the hydrologic process itself needs to be better defined.

OBJECTIVE: Develop hydrologic statistics within a regional context and identify the effect of persistence due to long-term climatic fluctuations.

APPROACH: Use the statistical theory of extremes and time-series analysis to analyze the distribution of flows as expressed through the spectrum of flow regimes. Consider several measures of persistence, treating this statistic as a random variable in itself, as well as giving it traditional treatment as a constant property of the underlying stochastic process. Examine empirical-flow information from both national and international data bases that will be developed for this project. Use other surrogate hydrologic records, such as dendrochronologic records, ice core records, and so forth, as needed and available.

PROGRESS: A U.S. Geological Survey streamflow data set has been defined for climatologic analysis. The data set is called the HCDN (Hydro-Climatic Data Network) and contains over 73,251 water years of record at 1,659 stations. The records were chosen for inclusion in the data set if (1) they were good quality discharge measurements, and (2) the streamflow reflected negligible anthropogenic impacts. The identification report with its accompanying information diskette has been published as U.S. Geological Survey Open-File Report 92-129. The data itself will be released on a CD-Rom, currently under preparation. The construction of the data set required not only stringent application of qualifying criteria but also extensive data checking and cleanup of the contents of the WATSTORE data files for the HCDN stations, and thus took an extended period of time even after appropriate records had been identified. The work was carried out with the encouragement of the Office of Surface Water and with the help of surface water specialists in each WRD district and state office. The data set was assembled for the purpose of studying climatic forcing and hydro-climatic interrelationships over the period for which measured streamflow records exist.

Extensive statistical and time series analysis has been carried out on the isotopic records obtained from vein calcite in Devils Hole, Nevada. Two reports—one on the dating of such cores with ^{230}TH-^{234}U-^{238}U mass spectrometer methods and the second, on the implications of the ^{18}O isotopic values as global climate records, in particular posing a challenge for the Milankovitch theory of the onset of glacial periods—have been published. Other aspects of these records are under study. A video report showing a summary of the National Water Conditions maps for the period of availability, U.S. Geological Survey Open-File Report 90–160, has been released: project chief was consultant on this effort.

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Landwehr, Jurate Maciunas, Tasker, Gary D., and Jarrett, Robert D., 1987, Relative accuracy of log-Pearson III procedures: American Society of Civil Engineers, Journal of Hydraulics Division, Proceedings, v. 113, no. 9, p. 1206–1210.

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TITLE: Continental Hydrology and Global Climate (NR 88–144)

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PROBLEM: The hydrology of the continents helps determine the global climate. The hydrosphere and the atmosphere are tightly coupled due to the role of water in the radiation and heat budgets of the atmosphere. Future progress in studies of global hydrology and climate dynamics will require interdisciplinary analyses of the dynamics of this coupled system.

OBJECTIVE: (1) Develop improved models of the global climate system by improving the parameterization of hydrologic response of the land surface in those models. (2) Develop an improved understanding of the global hydrologic cycle and its interlationship with global climate.

APPROACH: Much of the research uses the numerical climate model of the Climate Dynamics Project at the Geophysical Fluid Dynamics Laboratory of the National Oceanic and Atmospheric Administration. It is the subject of model development, and one of the tools for studying coupled dynamics.

PROGRESS: (1) The sensitivity of climate to evaporation from the continents was estimated by simulations using a mathematical model of the general circulation of the atmosphere. An analysis of the surface and atmospheric budgets of water and energy in the simulations revealed the processes by which the additional evaporation affects the atmosphere. One fundamental problem studied was the question of where additional evaporation returns to the earth as precipitation. In the tropics, this redistribution of water vapor was driven mainly by the prevailing circulation and its induced changes. With more water vapor cycling through the atmosphere, the Hadley circulation intensified and the monsoonal circulations were weakened. In the middle latitudes, the changes in vapor transport were associated instead with changes in the transient eddy fluxes of water, with a reduced onshore humidity gradient. At all latitudes, the effect of changes in transport was to export about half of the additional water vapor from the continents to the oceans.

(2) A system was established for the transfer of numerical output of climate-model experiments from this project to other interested scientists in the U.S. Geological Survey and elsewhere.

(3) In support of participation of the Geophysical Fluid Dynamics Laboratory in a multi-institution intercomparison of climate models, this project provided an updated scheme for parameterization of land-surface hydrology in its climate model.

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TITLE: Transport of Dissolved and Suspended Materials in Surface Waters (NR 90–147)

PERSONNEL: Jonathan Lee, Project Chief
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PROBLEM: Although a major effort has been made to understand the hydrodynamics of surface waters, less effort has been devoted to the study of transport mechanisms and to the development and validation of computational models for simulating the transport of dissolved and suspended materials. Recent progress in hydrodynamics has created additional opportunities for advances in surface-water transport. It may be possible to develop and validate more physically correct descriptions of transport processes in terms of flow characteristics than have been previously available. Microscale processes must be expressed at the macroscale level by algorithms which can be validated in computational models using laboratory and field data.

OBJECTIVE: (1) The evaluation of existing methods and techniques; (2) the development, or validation, or both, by the use of laboratory and field data, of algorithms describing dissolved- and suspended-material transport processes; (3) the development, or validation, or both, of computational techniques for solving the partial-differential equations describing surface-water transport processes; (4) the development and validation of multidimensional, computational models for the transport of dissolved and suspended materials in surface waters; and (5) the development of techniques for the application of computational, surface-water transport models to field problems.

APPROACH: Algorithms that quantify relationships between flow characteristics and transport processes will be selected from the literature or developed on the basis of concepts derived from the study of laboratory and field data. Computational schemes for the solution of the convective-dispersion equation in two and three dimensions will be analyzed for efficiency and accuracy. Advanced turbulence-closure schemes, necessary for the proper simulation of certain transport processes, will be studied in two- and three-dimensional models. Two- and three-dimensional flow and transport models will be developed for use in validating transport algorithms for both dissolved and suspended materials.

PROGRESS: Work continued on the development of depth-averaged hydrodynamic models for use as the basis for transport modeling. The finite-difference algorithm used for the momentum equations in TRIM, the two-dimensional, vertically averaged, surface-water flow model developed by Cheng and Casulli, was improved. These changes resulted in significantly less dissipation in results for flows in weakly forced or unforced basins. A Research Science Institute student, Gardenia Chavez, assisted with this work.

Development of a UNIX-based scientific, interactive, extensible, visualization environment (SIEVE), continued. SIEVE is based on the Graphical Kernel System (GKS), the X-Window system, and the Network Common Data Form (netCDF). SIEVE produces plots of input to and output from hydrodynamic/transport models. Two conference papers were presented on SIEVE by Gary Granger.

I extended work I had begun earlier on the effect of highway embankments on flow and circulation patterns in Port Royal Sound, South Carolina. This work demonstrated the utility of the Surface-Water, Integrated, Flow and Transport model (SWIFT2D) for analyzing the impact of human alterations of complex water bodies. By means of nested submodels, I quantified the changes in flow caused by the embankments and showed that one of the embankment openings created a jet which caused a significant change in circulation in Battery Creek, a branch of Port Royal Sound, during flood tides. I wrote a journal paper on this work with coauthors R.W. Schaffranek and R.A. Baltzer.

TITLE: Regional Water-Quality Assessment (NR 90–148)

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PROBLEM: Providing meaningful information on water quality at the national scale is a considerable scientific challenge. The problem is complex, because there is no "national water quality" in any true sense of the term. National water-quality issues are, in essence, common problems that manifest themselves differently among the Nation's diverse hydrologic systems. Meaningful national assessments must identify the commonalities among these settings and explain the differences. For this reason, traditional techniques that attempt simple statistical analysis of massive "national" data sets have met limited success. Considerable need exists for methods that examine regional water quality at a range of spatial and temporal scales and that aggregate the results across scales.

OBJECTIVE: The objectives of this research are to study human and climatic influences on the regional water quality of shallow aquifer and surface water-ground water systems, and to develop methods to aggregate results and draw conclusions at national and regional scales from studies of areas on the order of tens to hundreds of square kilometers.

APPROACH: The project has a major emphasis in comparative hydrology; the research will be accomplished largely through local scale studies of the National Water-Quality Assessment (NAWQA) Program where the opportunity exists to examine how processes affecting regional water quality differ among different hydrologic and climatic settings. The research agenda includes (1) examination of temporal and spatial variations in water quality relative to flow-system scale, climate, land-use patterns, etc., and inferring and testing the implications for network design, (2) studies of the effects of surface water-ground water interactions on regional water quality, (3) use of multivariate statistical procedures to classify shallow ground-water quality and to relate these to landscape features, and (4) development and testing of methods for assessing ground-water vulnerability to contamination.

PROGRESS: This past year the project has focused largely on preparation of a book on regional ground-water quality to serve as a reference/sourcebook on the design and interpretation of regional scale studies. The book will be completed in July 1992 and sent to the publisher, Van Nostrand Reinhold, at that time. In addition, a National Research Council committee report on techniques for assessing ground-water vulnerability to contamination is nearing completion. Preliminary work on sample-size estimation for regional ground-water quality surveys has been completed. A 5-week course on the design of regional ground-water quality studies was given for the Italian National Research Council.

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TITLE: Ice and Climate (WR 70-064)

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PROBLEM: The variations of the components of the cryosphere—sea ice, snowpacks, ice sheets, and glaciers—and their role in the hydrologic cycle and climate change (at daily seasonal and climatological time scales), both worldwide and regional, is essentially unknown. Two major technological advances which have occurred in the last decade now make it possible to attack this problem: (1) Satellite microwave sensors observe key cryospheric parameters on global scales at time intervals as short as 2 days. Also, new airborne microwave sensors provide observations with great spatial resolution and provide new information on the small-scale processes and their relationship with the large-scale processes. (2) Improved numerical models make it possible to use these space microwave data to perform cause and effect simulations of cryospheric variations.

OBJECTIVE: (1) Join in the design, calibration, and utilization of passive and active microwave satellites for cryosphere/climate research. This includes U.S. satellites and those of the European Space Agency, such as ERS-1 and TOPEX. (2) Design and perform sea ice experiments to acquire in situ and aircraft data to perform the satellite calibrations, and to use these results in sea ice models. (3) Acquire data to test the numerical models of the Arctic and Antarctic ice sheets and ice packs by directly participating in remote-sensing and surface-truth experiments and from remote-sensing polar-orbiting satellites. (4) Investigate the dynamics and thermodynamics of the upper ocean and their relation to the ice thickness, the results to be applied to the sea-ice cover models. (5) Investigate the use of satellite passive microwave data for snow water equivalent mapping for various areas, including the Upper Colorado River Basin, and China. (6) Construct multidimensional time-dependent models of glacier flow and ice-sheet flow and to test them with observations of glaciers.

APPROACH: (1) Continue the long-term joint sea ice programs with the National Aeronautics and Space Administration (NASA), the Nansen Environmental Remote Sensing Center (NERSC), the French Space Agency (CNES), and the European Space Agency (ESA). These programs involve a three-level approach with simultaneous ice observations by satellite, aircraft, and surface teams. (2) Participate in the design of microwave sensors for satellite missions and in the subsequent analysis and use of the data. (3) Participate in the planning and performance of aircraft remote sensing missions. (4) Participate in surface-truth experiments on snowpacks, sea ice, and ice sheets. (5) Continue both the 20-year data collection program at the South Cascade Glacier and the aerial reconnaissance of western North American glaciers. (6) Develop models for sea ice, glacier, and ice sheet dynamics.

PROGRESS: Sea Ice.—Carried out the Seasonal Ice Zone Experiment (SIZEX)-1992 winter field program. SIZEX is a European Space Agency (ESA) program, and the 1992 experiment was the key ocean/ice post-launch experiment for the first European Research Satellite (ERS-1). This experiment used real-time ERS-1 Synthetic Aperture Radar (SAR) observations of the seasonal ice zone to guide the in situ sampling program. Completed the analysis of the 9-year Scanning Multichannel Microwave Radiometer (SMMR) observations of the Arctic and Antarctic sea ice, which will be published in October 1992 as NASA Special Publication 511.

Snow.—The joint U.S. Geological Survey, National Aeronautics and Space Administration, and U.S. Department of Agriculture passive microwave snow research program continues to demonstrate and develop new techniques for the remote sensing of snow from space. The National Oceanic and Atmospheric Administration's (NOAA) National Operational Hydrologic Remote Sensing Center is now using a passive microwave algorithm, developed by this project, to supplement the Center's snow cover products. Using only the SMMR observations, we have has generated a snowpack climatology, from 1979 to 1986, for the Upper Colorado River Basin. We found that a spatial integral of the winter SMMR observations alone give a strong index of the following spring flow in the Colorado River. The index was improved when digital elevation data was incorporated into the analysis. A paper on this subject was presented at an International Glaciological Society on Remote Sensing and will appear in the Annals of Glaciology. We continued to collect internal snowpack data from index sites in the basin. The grain size data from these observations are now being recognized as important in determining the regional passive microwave snowpack signatures.

Ice Sheets.—The second field season of the National Science Foundation-funded project to study the structure and evolution of the west Antarctic Icesheet (ALICE: Airborne Lithosphere and Ice Cover Experiment) was successfully completed. A laser altimeter was successfully added to the research aircraft and over 25,000 km of data lines were flown. Data analysis is now underway, and preliminary results have shown the presence of an under-ice volcano.

Glaciers.—At South Cascade Glacier, the two-decade-long program of mass balance data continues, which has shown record negative mass balance for the past 3 years. At Hubbard Glacier, in cooperation with the Alaska District Office, we maintained camera sites and obtained sequential oblique photography of the terminus, and we have observed that the terminus is advancing rapidly. At Columbia Glacier, we continue to monitor the drastic retreat.

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SURFACE-WATER HYDROLOGY

TITLE: Hydrodynamics and Mathematical Modeling of Circulation and Transport Phenomena in Tidal Estuaries (WR 76–140)

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PROBLEM: The ecosystem of a tide-affected estuary consists of an extremely complicated balance of natural processes and human-induced activities. Some of the basic characteristics of such a system, for example, the San Francisco Bay estuarine system, are not well understood. A comprehensive description of the hydrodynamics and the related transport phenomena is still lacking. A better understanding of the effects among the interactive natural and human-induced processes on this system requires advances in basic science relating the physical, chemical, and biological estuarine processes. Circulation in a tidal estuary is generated in response to astronomical tides, inflow of freshwater, winds, and stratification due to salinity. The basin topography (bathymetry), air-water interaction, water-sedimentation interface, mixing characteristics, frictional loss at the bottom, and the rotational effects of the earth, together with the above-mentioned driving forces, constitute an extremely complicated balance that conserves mass, momentum, energy, and conservative solutes in the system.

OBJECTIVE: (1) Understand processes and rates by which water, salt, and other solutes interact; (2) develop methods to enable quantification of the relative importance of river inflow, winds, tides and other dynamic forcings that act upon the system; and (3) develop and verify conceptual and numerical models of these interactions.

APPROACH: Include intensive field-data collection and mathematical-model development and implementation in project activities. Collect long-term current and stage data. Develop effective methods of solution to the equations that govern the basic hydrodynamic processes, that is, the conservation equations of mass, momentum, energy, and salt. Treat field data-collection and numerical-modeling research as complementary parts of a well-integrated program; use field data to calibrate and verify numerical models, and use numerical-model results to guide future data-collection activities. Use numerical models as research tools for investigations of short- and long-term transport phenomena after the models are calibrated and verified.

PROGRESS: This project continues to provide technical guidance and support to the Interagency study of San Francisco Bay/Delta. Significant progress has been made in both two-dimensional (2-D) and three-dimensional (3-D) estuarine hydrodynamic modeling research. A depth-averaged, Tidal, Residual, and Intertidal Mudflat model (TRIM), was developed in collaboration with Professor Vincenzo Casulli of the University of Trento, Trento, Italy. The 2-D TRIM model has been calibrated and verified against an extensive data set collected in San Francisco Bay in 1979-1980. Using the TRIM model as a research tool, the hydrodynamic characteristics of San Francisco Bay have been defined and reported in a manuscript to be submitted for journal publication (presently in review). The formulation and the numerical methods used in the 3-D TRIM model has been reported at Estuarine and Coastal Modeling Conference, and a full length paper has been accepted for publication by the Internal Journal for Numerical Method in Fluids. The Project Chief collaborates with Jon Burau of California District Office on the continuing developments of pre- and post-processing programs for the TRIM modeling system. This modeling system will be used in District estuarine programs, thus it serves as the bridge of technology transfer. We have been asked to participate in two demonstration projects using the TRIM modeling system. An exhibit to show the tides and the transport of salinity in San Francisco Bay will be open at the Oakland Museum in the fall of 1992. This exhibit uses our model results to demonstrate properties of the Bay's hydrodynamics to the general public. Another exhibit which is designed to demonstrate the U.S. Geological Survey latest research findings on hydrodynamics of San Francisco Bay will be on display at the U.S. Army Corps of Engineers Visitor Center in Sausalito, California. The model results will be displayed on a high performance graphics workstation, the contents of the display will be highly technical. Thus, this exhibit shows the USGS research efforts in promoting our understanding the hydrodynamic processes in San Francisco Bay. Both of these projects will be delivered within FY 1992.

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TITLE: Research Vessel Polaris Operations in San Francisco Bay and Adjacent Coastal Ocean (WR 77-156)

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PROBLEM: A stable moving platform is needed to house at least 10 scientists throughout the year (for periods of weeks) so that large volumes of complex and continuous data can be carefully and rapidly collected and precisely measured and analyzed immediately after collection.

OBJECTIVE: Provide scientific platform (research vessel) for estuarine studies, platform functions, and measurement, collection, and subsequent analysis of geological, chemical, physical, and biological data throughout the year for extended time periods.

APPROACH: Provide support for research vessel, including operating support for dockage fees, boat maintenance, diesel fuel, and food for scientists and crew.

PROGRESS: Provided research vessel support for routine field sampling by personnel in several projects within the Branch of Regional Research (WR) and the California District. For example, the POLARIS has been used in the "San Francisco Bay River-Estuary Toxic Contaminant Study."

TITLE: Analysis and Modeling of Conservative and Nonconservative Transport Processes (WR 83-183)

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PROBLEM: The biological and chemical characteristics of aquatic environments depend on a generally complicated balance of physical, chemical, and biological processes. Basic to describing these characteristics is an understanding of transport processes including both advection and mixing. For a given water body, these processes depend heavily on the mass, momentum, and energy transfers at boundaries and the internal response of the system. Many of these transfers and responses are poorly understood.

OBJECTIVE: Broad goals of this project are to quantitatively understand the physical processes responsible for the transport of conservative and nonconservative solutes of biological and chemical importance. Through the use of time series analysis and other methods, conceptual, statistical, and numerical models of these processes are being developed.

APPROACH: Use data analysis, including the application of digital filters, to examine daily to interannual time-scale phenomena, spectral analysis, empirical orthogonal function analysis, and regression analysis and numerical models. Use numerical models, including box and finite-element models, in one, two, and three dimensions.

PROGRESS: Development of a three-dimensional finite element tidal and residual circulation model and finite element network generation software has allowed a quantitative analysis of circulation in several estuaries and coastal seas. Emphasis has been placed on salinity intrusion into Delaware Bay and River where salt flux processes have been examined in detail.

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TITLE: Coupled Transport and Geochemical Processes Determining the Fate of Chemicals in Surface Waters (WR 84-187)

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PROBLEM: Coupled transport and biogeochemical processes determine the fate of chemicals both naturally present in surface waters and those introduced through anthropogenic activities. In mountainous environments, coupled processes operate at scales which can be years and kilometers in watersheds or minutes and decimeters in the hyporheic zone. Although individual processes are often well understood in isolation, the ability to quantify chemical fate across the stream-watershed continuum requires development in design of field experiments and mechanistic formulations to integrate interpretation of multiple processes.

OBJECTIVE: Develop experimental field techniques and mechanistic formulations to quantitatively identify rates and extents of transport within the stream-watershed continuum. Focus on transport processes which most influence the fate of chemicals introduced from the surrounding watershed into pristine streams (for example, natural dissolved organic materials and nutrients, as well as, acid mine drainage).

APPROACH: Cooperate with hydrologists, geochemists, and ecologists to identify the processes of environmental fluid mechanics exerting significant influence on the fate of chemicals in mountainous watersheds. Study these processes (for example, transient storage of solutes in the hyporheic zone) specifically to estimate hydrologic parameters needed for quantitative determinations of solute transport. Dynamic field experimentation is the primary mode of study, augmented with detailed sampling studies and numerical simulations.

PROGRESS: In the acid mine drainage St. Kevin Gulch, Colorado, variation in streambed topography causes localized recharge of streamwater along well-defined substream flow paths in the hyporheic zone. The substream flow paths maintain the stream-watershed continuum for solute transport. Measurements of groundwater heads, tracer movement through the hyporheic zone, and simulations of steady-state flow support this identification of substream flow paths. Improved assessments of iron removal from the stream channel have resulted from collaboration with the Center for Advanced Decision Support for Water and Environmental System

(CADSWES) in Colorado to develop capabilities for simulation analysis within the Modular Hydrologic Modeling System. (Leadville, Colorado—Upper Arkansas River Toxic Substances Hydrology Site; J. Harvey, Zellweger, and Bencala working with McKnight, Kimball, Broshears, and Runkel). In the Snake River watershed (Summit County, Colorado) Boyer and Hornberger (University of Virginia), have collaborated with Bencala and McKnight to apply the TOPMODEL watershed topography concepts to identifying source zones of dissolved organic material.

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TITLE: Fluvial Processes and River Mechanics (WR 83–194)

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PROBLEM: Many difficult problems in river mechanics may have stemmed from inadequate understanding of the multiplicity and interaction of fluvial processes. Some of the problems may have been solved, but in a very simplified, approximate way. Many efforts have been directed, but without apparent success, to fully account for the causes, occurrences, and mechanisms of catastrophic events, such as flash floods, debris flows, and channel changes resulting from torrential storms, sudden snow or glacier melt, dam break, volcanic eruptions, and earthquakes. Such failures may be partially attributed to the deficiency and incompleteness of existing empirical formulas (or models) representing the relationships between various processes and responses.

OBJECTIVE: Seek a full understanding of various fluvial processes on hillslopes and in river channels, which undergo changes in response to rapid disturbances, such as torrential storms, sudden snow or glacier melt, dam break, volcanic eruptions, and earthquakes. Improve or generalize existing empirical formulas that do not accurately describe the process-response relationships. Develop new relationships for various soils and highly-concentrated sediment-water mixtures, such as those posed in the form of rheological or constitutive equations. Build mathematical models, using such relationships, for flash floods, debris flows, channel changes, and so forth. Ultimately apply these models to minimize the loss of life and property that may result from such catastrophic events.

APPROACH: Assess the validity and applicability of existing formulas for various fluvial processes, such as rainfall, infiltration, runoff, and sediment movement (erosion and deposition) on hillslopes and in river channels. Modify or generalize the existing formulas to the utmost extent that they will become more representative under a wider spectrum of field conditions. Formulate rheological or constitutive equations for various soils and highly-concentrated sediment-water mixtures, and determine the values of rheological parameters and material constants using available field or laboratory data. Build mathematical models for flash floods, debris flows, channel changes, etc. and solve them on digital computers using optimum numerical schemes. Verify the models using actual events.

PROGRESS: Debris-flow research has progressed in theoretical and experimental phases. Significant results in the theoretical phase have been the analytical expressions of theoretical velocity profiles for debris flow simulated in the conveyor-belt flume and the ring-shear apparatus based on a simplified version of the generalized viscoplastic fluid (GVF) model. We have compared the theoretical velocity profiles with measured ones obtained from experiments, thereby evaluating the rheological parameters of a simulated debris flow. In the experimental phase, data were acquired and analyzed from debris-flow experiments conducted at the University of California-Berkeley. Data having been obtained so far consist of a set of (1) measured velocity profiles and flow profiles with or without a snout in the conveyor-belt flume for dry flows of 5- or 14-mm glass spheres and (2) measured velocity profiles, average shear and normal stresses on the shearing plane, and volume change, if any, of the tested sample in the ring-shear apparatus for dry flows of 3- or 5-mm glass spheres. An analysis of experimental results has indicated that data on the solids volume fraction (or concentration) distribution of glass spheres in addition to the velocity profile are needed if all the rheological parameters are to be completely evaluated. Continued efforts have been made to measure or evaluate the particle concentrations in the flow, but so far without much success. Other areas of research in progress are: (1) the further evaluation of power laws for flow resistance in terms of Coles' wake law, (2) the formulation of criteria for free-surface instability in clear-water laminar and turbulent flows as well as in debris flows, (3) the two-phase flow theory applied to modeling stratified sediment gravity flow, and (4) the development of a "layered-flow" theory for gravity-induced granular flows.

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Ling, C.H., Chen, C.L., and Jan, C.D., 1990, Rheological properties of simulated debris flows in the laboratory environment: International Symposium on the Hydraulics and Hydrology of Arid Lands, American Society of Civil Engineers, San Diego, California, [Proceedings], p. 218–224.

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Ling, C.H., Jan, C.D., Chen, C.L., and Shen, H.W., 1992, Numerical simulation of a sphere moving down an incline with identical spheres placed equally apart: Conference on Engineering Mechanics, American Society of Civil Engineers, 9th, College Station, Tex., [Proceedings], p. 764–767.

TITLE: Mathematical Modeling Principles (WR 73-197)

PERSONNEL: James P. Bennett, Project Chief
Maria M. Watta, Secretary

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PROBLEM: The development of models of hydrologic systems requires the description of individual processes in mathematical terms and the solution of sets of complex equations in differential form. Research is needed on application of mathematical theory to the modeling of transport of sediments, including mudflows and hyperconcentrations such as occur after natural disasters such as volcanic eruptions or dam failures.

OBJECTIVE: Develop mathematical descriptions of flow and water-quality processes that can be linked together to form models of hydrologic systems. Develop mathematical techniques for efficient solution of equations on digital computer. Develop techniques for studying sensitivity of parameters.

APPROACH: The approach to the problem will be by theoretical study, model development, and model testing.

PROGRESS: Conceptualized and coded an eddy-zone sand storage model for rivers such as the Colorado in Grand Canyon with severe constrictions. Computed long-term sediment budgets for upper and lower segments of the Colorado River, Grand Canyon, Arizona. The eddy-zone model enabled determination of sensitivity of the relative amounts of channel and eddy-zone storage to mode of operation of Glen Canyon Dam. Problems with nonlinearites in allocation of transport capacity among sand sizes in stream power-based sediment transport model were determined to make it unsuitable for use for smaller sizes in situations where unlimited amounts of bed-material are exposed to stream currents. Coordinated USGS efforts in Colorado River-Glen Canyon Dam environmental impact investigation through preparation of phase I reports. Began development of a multi-size sand transport model based on general physics of flow in one-dimensional channels.

REPORTS PUBLISHED 1987–1992:

Bennett, J.P., 1988, Simulation of transport-related properties, *in* Bradford, W.L., and Horowitz, A.J., eds, The role of sediments in the chemistry of aquatic systems—Proceedings of the sediment chemistry workshop, February 8–12, 1982: U.S. Geological Survey Circular 969, 64–75.

TITLE: Resolution of Hydroclimatic Uncertainty (WR 89-201)

PERSONNEL: Marshall E. Moss, Project Chief
Ana M. MacKay, Administration Operations Assistant
Douglas Wellington, Computer Program Analysist
David A. Pratt, Student, (University of Arizona)

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PROBLEM: There is a great deal of uncertainty about future climates on a decadal scale. This uncertainty has strong implications on the water-resources planning and management decisions that are being made now and will be made in the future. Information about the hydrologic implications of climate uncertainty is minimal.

OBJECTIVE: Develop technology that can be used to evaluate hydrologic information generated by climate models and to incorporate that information into strategies for monitoring the potential hydrologic effects of climate change.

APPROACH: Use a combination of geostatistics and Bayesian models of data errors to develop a data base of hydrologic variables aggregated at the spatial scales of the climate models. Use these data to evaluate the information content of the hydrologic components of existing climate models. Incorporate significant information into a scheme for monitoring regional hydrologic effects of climate change.

PROGRESS: The validity of Kriging variances as an estimator of the errors of estimation of areal precipitation at the spatial scale of a general circulation model (GCM) was investigated by a resampling scheme that used actual precipitation data. For both purely random sampling and random-stratified sampling, the Kriging variance was found to under-estimate the variance of the errors if only data from within a GCM cell were used to estimate precipitation at ungaged sites. However, if data surrounding the cell also were used in the estimation, Kriging variances over-estimated the actual error variances. Only small decreases in the error of estimation of precipitation were found for random-stratified sampling relative to random sampling if 32 precipitation stations were available within the GCM cell.

Studies of the changes in information content of precipitation outputs of GCMs with changing spatial scales of the model were initiated. It was found that aggregation of outputs along a band of constant latitude (zonal averaging) gave increased information only about 70 percent of the time, and that for the remainder of the time, aggregation can result in significant degradation of information.

The study of climate change in the Delaware River basin was extended to investigate the sensitivities of the water supplies of New York City and Philadelphia to potential climate change and how these sensitivities could be lessened by modifying the operating rules of the river system. Under the current operating rules, the New York water supply is much more sensitive to climate change, but this situation can be assuaged by adjusting the rules with little or no loss to the Philadelphia water supply.

REPORTS PUBLISHED 1989–1992:

Moss, M.E., and Tasker, G.D., 1990, Manual for comparing methods of designing hydrologic-data-collection networks: U.S. Geological Survey Open-File Report 90-389, 104 p.

____1991, An intercomparison of hydrological network-design technologies: Hydrological Sciences Journal, v. 36, no. 3, p. 209-221.

____1991, Hydrologic implications of climate uncertainty in the western United States: Proceedings of Colloquium on Managing Water Resources under Conditions of Climatic Uncertainty, National Academy Press, Washington, D.C., p. 148–157.

____1992, Bayesian relative information measure—a tool for analyzing the outputs of general circulation models: Journal of Geophysical Research, v. 97, no. D3, p. 2743-2756.

APPENDIXES

APPENDIX 1.—Alphabetical Listing by Project Chief

PROJECT CHIEF	DISCIPLINE	PROJECT NUMBER	PROJECT TITLE	PAGE
Alley, William M.	SW Hydrology	NR 90-148	Regional Water-Quality Assessment	349
Andrews, Edmund D.	Geomorphology/ Sediment Transport	CR 82-273	River Mechanics	87
Averett, Robert C.	Ecology	CR 88-312	Ecological Interactions of Lakes and Stream	19
Back, William	GW Chemistry	NR 57-034	Spatial Distribution of Chemical Constituents in Ground Water	127
Baedecker, Mary Jo	GW Chemistry	NR 83-129	Comparative Study of Organic Degradation in Selected Hydrogeologic Environments	148
Baltzer, Robert A.	SW Hydrology	NR 69-019	Numerical Simulation of Hydrodynamic Processes in Rivers, Estuaries, and Coastal Embayments	328
Bencala, Kenneth E.	SW Hydrology	WR 84-187	Coupled Transport and Geochemical Processes Determining the Fate of Chemicals in Surface Waters	364
Bennett, James P.	SW Hydrology	WR 73-197	Mathematical Modeling Principles	371
Benson, Larry V.	SW Chemistry	CR 82-207	Arid Regions Climate and Chemistry	273
Betancourt, Julio	Ecology	WR 76-145	Biotic Response to Climatic Variability and Human Impacts in Arid Lands	58
Bredehoeft, John D.	GW Hydrology	WR 75-176	Water Wells as Strain Meters	235
Bricker, Owen P.	SW Chemistry	NR 81-109	Geochemical Cycling of Trace Elements and Nutrients in Natural Water Systems	300
Brown, Charles E.	GW Hydrology	NR 84-130	Multivariate Statistical Techniques for Assessing Regional Ground-Water Quality and Quantity	215
Callender, Edward	SW Chemistry	NR 76-065	Sedimentary Geochemical Processes Affecting the Exchange of Nutrients and Transition Metals Between Sediment and Water in Riverine, Estuarine, and Lacustrine Environments	291
Campbell, William J.	SW Hydrology	WR 70-064	Ice and Climate	352
Carter, Virginia P.	Ecology	NR 73-090	Remote Sensing and Ecological Research in Wetlands	33

PROJECT CHIEF	DISCIPLINE	PROJECT NUMBER	PROJECT TITLE	PAGE
Getzen, Rufus T.	GW Hydrology	WR 76-171	Hydrologic Analysis of Petrofabrics—Sandstones	234
Godsy, Edward M.	Ecology	WR 71-068	Fate of Organic Chemicals in Subsurface Environments	52
Goerlitz, Donald F.	GW Chemistry	WR 84-189	Chemistry of Aquatic Organic Matter	175
Goldberg, Marvin C.	SW Chemistry	CR 76-199	Water Chemistry of Sediment Surface Coatings	269
Harvey, Ronald W.	Ecology	CR 91-327	Interaction of Bacteria with Environmental Contaminants and Solid Surfaces in the Aquatic Environment	27
Hem, John D.	SW Chemistry	WR 57-076	Chemistry of Hydrosolic Metals and Related Constituents of Natural Water	306
Herkelrath, William N.	GW Hydrology	WR 82-179	Nonisothermal Multiphase Flow	239
Hsieh, Paul A.	GW Hydrology	WR 83-184	Hydrology of Fractured Rocks	245
Hupp, Cliff R.	Ecology	NR 90-145	Vegetation and Hydrogeomorphic Relations	41
Ingebritsen, Steven E.	GW Hydrology	WR 74-121	Hydrologic Studies of Heat and Mass Transport	229
James, Ronald V.	GW Chemistry	WR 68-036	Factors Determining Solute Transfer in the Unsaturated Zone	157
Jarrett, Robert D.	SW Hydrology	CR 90-321	Paleohydrology and Climate Change	326
Jones, Blair F.	GW Chemistry	NR 69-020	Mineral-Water Interaction in Saline Environments	124
Kendall, Carol	GW Chemistry	WR 91-080	Stable Isotope Tracers of Biogeochemical and Hydrologic Processes	163
Kharaka, Yousif K.	GW Chemistry	WR 76-139	Geochemistry of Water in Fine Grained Sediments	167
Kipp, Kenneth L.	GW Hydrology	CR 85-292	Ground-Water Solute-Transport Simulation.	200
Konikow, Leonard F.	GW Hydrology	NR 81-120	Digital Modeling of Transport in the Saturated Zone	212

PROJECT CHIEF	DISCIPLINE	PROJECT NUMBER	PROJECT TITLE	PAGE
Kraemer, Thomas F.	GW Chemistry	NR 82-138	Uranium-Thorium Series Radioisotopes in Ground-Water and Surface-Water Systems .	153
Kuwabara, James S.	Ecology	WR 86-190	Solute Transport Involving Biological Processes in Surface Waters	73
LaBaugh, James W.	Ecology	CR 85-293	The Role of Chemical Fluxes in the Biogeochemistry of Inland Surface Waters, Including Lakes, Reservoirs, and Wetlands	13
Lai, Vincent C.	SW Hydrology	NR 79-096	Computational Hydraulics for Surface Water Problems	332
Landa, Edward R.	SW Chemistry	NR 78-092	Hydrogeochemical Controls on the Migration of Radionuclides from Uranium Mill Tailings	294
Landwehr, Jurate M.	SW Hydrology	NR 84-133	Regional Hydrologic Processes	342
Leavesley, George H.	SW Hydrology	CR 77-228	Precipitation-Runoff Modeling of Watershed System	314
Lee, Jonathan	SW Hydrology	NR 90-147	Transport of Dissolved and Suspended Materials in Surface Waters	347
Leenheer, Jerry A.	SW Chemistry	CR 84-285	Comprehensive Organic Analysis of Water..	284
Leland, Harry V.	Ecology	CR 92-337	Effects of Toxic Substances on Aquatic Communities	31
Lovley, Derek R.	Ecology	NR 87-136	Modeling of Microbially Catalyzed Geochemical Reactions in Aquatic Environments	37
Luoma, Samuel N.	Ecology	WR 75-125	Availability of Trace Elements in Sediments to Aquatic Organisms	54
Malcolm, Ronald L.	SW Chemistry	CR 68-046	Origin, Characterization, and Quantification of Natural Organic Solutes in Water	256
Mariner, Robert H.	GW Chemistry	WR 79-165	Chemical and Isotope Studies of Thermal Waters of the Western United States	171
Marzolf, G. Richard	Ecology	CR 91-325	Limnological Phenomena in Impounded Rivers	25

PROJECT CHIEF	DISCIPLINE	PROJECT NUMBER	PROJECT TITLE	PAGE
McKnight, Diane M.	Ecology	CR 84-286	Interactions Between Organic Solutes and Trace Metals in Natural Waters, and Their Ecological Role	8
Meade, Robert H.	Geomorphology/ Sediment Transport	CR 87-309	Sediment-Transported Pollutants in the Mississippi River	91
Meade, Robert H.	Geomorphology/ Sediment Transport	CR 75-102	Movement and Storage of Sediment in River Systems	80
Milly, Chris D.	SW Hydrology	NR 88-144	Continental Hydrology and Global Climate	345
Moench, Allen F.	GW Hydrology	WR 75-127	Analytical Modeling of Flow and Transport in Aquifers and Geothermal Reservoirs	232
Moss, Marshall E.	SW Hydrology	WR 89-201	Resolution of Hydroclimatic Uncertainty	373
Naff, Richard L.	GW Hydrology	CR 90-319	Application of Stochastic Processes in Hydrogeology	204
Neuzil, Christopher E.	GW Hydrology	NR 81-035	Hydrologic Behavior of Cretaceous Shales	207
Nichols, Frederic H.	Ecology	WR 86-192	Environmental Influences on Estuarine Benthic Community Dynamics	76
Nimmo, John R.	GW Hydrology	WR 89-198	Physical Characteristics that Determine Flow in the Unsaturated Zone	250
Nordstrom, Darrell K.	GW Chemistry	CR 92-326	Chemical Modeling and Thermodynamic Data Evaluation of Major and Trace Elements in Acid Mine Waters and Ground Waters	120
Oremland, Ronald S.	Ecology	WR 81-174	Microbial Biogeochemistry of Aquatic Environments	67
Osterkamp, Waite R.	Geomorphology/ Sediment Transport	CR 79-311	Sediment Impacts from Disturbed and Undisturbed Lands	94
Paillet, Frederick L.	GW Hydrology	CR 64-140	Borehole Geophysics as Applied to Geohydrology	187
Parkhurst, David L.	GW Chemistry	CR 89-318	Reaction-Transport Modeling in Ground-Water systems	117
Pereira, Wilfred E.	SW Chemistry	WR 83-204	Origin, Fate, and Transport of Organic Compounds in Surface and Ground Waters and Their Effect on Water Quality	309

PROJECT CHIEF	DISCIPLINE	PROJECT NUMBER	PROJECT TITLE	PAGE
Peterson, David H.	Ecology	WR 68-046	Geochemistry of Riverine and Estuarine Waters	48
Plummer, L. Niel	GW Chemistry	NR 76-056	Kinetics and Thermodynamics of Chemical Evolution in Ground-Water Systems	133
Rathbun, Ronald E.	SW Hydrology	CR 77-301	Transport and Degradation of Organic Substances in Streams	323
Reddy, Michael M.	SW Chemistry	CR 83-284	Aqueous crystal growth and dissolution kinetics of earth surface minerals	280
Reilly, Thomas	GW Hydrology	NR 91-152	Quantitative Analysis of Heterogeneous Hydrogeologic Controls on ground-water flow and transport	219
Rubin, Jacob	GW Hydrology	WR 82-180	Theories of Water Flow and of Solute Transport in the Unsaturated Zone	242
Sanford, Ward	GW Hydrology	NR 91-153	Reaction-Transport Phenomena in Hydrogeologic Settings	222
Schaffranek, Raymond W.	SW Hydrology	NR 80-104	Simulation Modeling of Hydrodynamic Systems	336
Seeley, James	SW Chemistry	CR 89-316	Solid Phase Chemistry and Related Environmental Processes	289
Shapiro, Allen M.	GW Hydrology	NR 84-134	Transport Phenomena in Fractured Rock	217
Simon, Nancy S.	SW Chemistry	NR 86-135	Distribution and Speciation of Metals in Sedimentary Environments	303
Slack, Keith V.	Ecology	WR 61-012	Limnology: Controls on Distribution and Composition of Benthic Communities of Inland Aquatic Ecosystems	45
Smith, J. Dungan	Geomorphology/ Sediment Transport	CR 91-324	Applications of Fluid and Sediment Mechanics to Basin and Regional Scale Hydrologic and Geomorphic Problems	101
Smith, Richard L.	Ecology	CR 86-295	Microbial Transformation of Dissolved Organic Carbon in Aquatic Environments	15
Sorey, Michael L.	GW Hydrology	WR 72-108	Technical Coordination and Support of Water Resources Division Geothermal Studies	228

TOPIC	PROJECT CHIEF	PROJECT NUMBER	PAGE NUMBER
Acid rain:	Bricker, Owen P.	NR109	300
	Malcolm, Ronald L.	CR046	256
	Reddy, Michael M.	CR284	280
Acid Mine Drainage:	Bencala, Kenneth E.	WR187	364
	Kipp, Kenneth L.	CR292	200
	McKnight, Diane M.	CR286	8
	Nordstrom, Darrell K.	CR326	120
Aquatic Habitat:	Andrews, Edmund D.	CR273	87
	Averett, Robert C.	CR312	19
	Carter, Virginia P.	NR090	33
	Cloern, James E.	WR164	62
	Hupp, Cliff R.	NR145	41
	Leland, Harry V.	CR337	31
	Luoma, Samuel N.	WR125	54
	Marzolf, G. Richard	CR325	25
	McKnight, Diane M.	CR286	8
	Nichols, Frederic H.	WR192	76
	Slack, Keith V.	WR012	45
	Triska, Frank J.	WR186	70
Carbon Cycle:	Betancourt, Julio L.	WR145	58
	Bricker, Owen P.	NR109	300
	Cloern, James E.	WR164	62
	Kendall, Carol	WR080	163
	Leenheer, Jerry A.	CR285	284
	Lovley, Derek R.	NR136	37
	McKnight, Diane M.	CR286	8
	Oremland, Ronald S.	WR174	67
	Reddy, Michael M.	CR284	280
	Stallard, Robert F.	CR313	98
	Streigel, Robert G.	CR320	32
	Sundquist, Eric T.	NR099	297
	Thorstenson, Donald C.	NR093	143
	Weeks, Edwin P.	CR200	196
Climate:	Benson, Larry V.	CR207	273
	Betancourt, Julio L.	WR145	58
	Campbell, William J.,	WR064	352

TOPIC	PROJECT CHIEF	PROJECT NUMBER	PAGE NUMBER
	Coplen, Tyler B.	NR064	138
	Jarrett, Robert D.	CR321	326
	Kendall, Carol	WR080	163
	Landwehr, Jurate M.	NR133	342
	Leavesley, George H.	CR228	314
	Milly, P.C.D.	NR144	345
	Moss, Marshall E.	WR201	373
	Peterson, David H.	WR046	48
	Webb, Robert H.	WR200	104
	Weeks, Edwin P.	CR200	196
	White, Arthur F.	WR196	178
	Winograd, Isaac J.	NR041	131
Estuaries:	Baltzer, Robert A.	NR019	328
	Carter, Virginia P.	NR090	33
	Cheng, Ralph T.	WR140	357
	Cloern, James, E.	WR164	62
	Conomos, T. John	WR156	361
	Kuwabara, James S.	WR190	73
	Luoma, Samuel N.	WR125	54
	Nichols, Frederic H.	WR192	76
	Peterson, David H.	WR046	48
	Schaffraneck, Raymond W.	NR104	336
	Walters, Roy A.	WR183	362
Fractured Rock:	Hsieh, Paul A.	WR184	245
	Paillet, Frederick L.	CR140	187
	Shapiro, Allen M.	NR134	217
	Winter, Thomas C.	WR090	184
	Wood, Warren W.	NR122	145
Geochemistry Isotopic tracers:	Coplen, Tyler B.	NR064	138
	Kendall, Carol	WR080	163
	Kharaka, Yousif K.	WR139	167
	White, Arthur F.	WR196	178
Geophysics:	Brown, Charles E.	NR130	215
	Paillet, Frederick L.	CR140	187

TOPIC	PROJECT CHIEF	PROJECT NUMBER	PAGE NUMBER
Geothermal Resources:	Sorey, Michael L.	WR102	226
	Sorey, Michael L.	WR108	228
	Mariner, Robert H.	WR165	171
	Ingebritsen, Steven E.	WR121	229
	Kharaka, Yousif K.	WR139	167
	Paillet, Frederick L.	CR140	187
Ground-water Flow Transport and Reactions:	Baedecker, Mary Jo	NR129	148
	Bredehoeft, John D.	WR176	235
	Davis, James A., III	WR065	159
	Eberl, Dennis D.	CR276	110
	Essaid, Hedeff I.	WR199	252
	Herkelrath, William N.	WR179	239
	Jones, Blair F.	NR020	124
	Kharaka, Yousif K.	WR139	167
	Kipp, Kenneth L.	CR292	200
	Konikow, Leonard F.	NR120	212
	Neuzil, Christopher E.	NR035	207
	Nordstrom, Darrell K.	CR326	120
	Parkhurst, David L.	CR318	117
	Plummer, L. Niel	NR056	133
	Reilly, Thomas E.	NR152	219
	Rubin, Jacob	WR180	242
	Sanford, Ward	NR153	222
	Sorey, Michael L.	WR102	226
	Thorstenson, Donald C.	NR093	143
	Voss, Clifford I.	NR089	209
	Wagner, Brian J.	WR178	237
	Weeks, Edwin P.	CR200	196
	White, Arthur F.	WR196	178
Grounds-water Hydraulics:	Bredehoeft, John D.	WR176	235
	Essaid, Hedeff I.	WR199	252
	Herkelrath, William N.	WR179	239
	Hsieh, Paul A.	WR184	245
	Konikow, Leonard F.	NR120	212
	Moench, Allen F.	WR127	232
	Neuzil, Christopher E.	NR035	207
	Paillet, Frederick L.	CR140	187

TOPIC	PROJECT CHIEF	PROJECT NUMBER	PAGE NUMBER
	Reilly, Thomas E.	NR152	219
	Shapiro, Allen M.	NR134	217
	Voss, Clifford I.	NR089	209
Hydrogeology:	Back, William	NR034	127
	Bredehoeft, John D.	WR176	235
	Getzen, Rufus T.	WR171	234
	Hsieh, Paul A.	WR184	245
	Ingebritsen, Steven E.	WR121	229
	Jones, Blair F.	NR020	124
	Konikow, Leonard F.	NR120	212
	Neuzil, Christopher E.	NR035	207
	Plummer, L. Niel	NR056	133
	Reilly, Thomas E.	NR152	219
	Shapiro, Allen M.	NR134	217
	Voss, Clifford I.	NR089	209
	Weeks, Edward P.	CR200	196
	Winograd, Isaac J.	NR041	131
	Winter, Thomas C.	CR090	184
	Wood, Warren W.	NR122	145
Lakes:	Averett, Robert C.	CR312	19
	Averett, R.C./Winter, T.C.	CR323	23
	Benson, Larry V.	CR207	273
	Callender, Edward	NR065	291
	Cloern, James E.	WR164	62
	Kuwabara, James S.	WR190	73
	LaBaugh, James W.	CR293	13
	Oremland, Ronald S.	WR174	67
	Striegl, Robert G.	CR320	21
	Winter, Thomas C.	CR090	184
	Wood, Warren W.	NR122	145
Metals:	Callender, Edward	NR065	291
	Davis, James A., III	WR065	159
	Hem, John D.	WR076	306
	Hupp, Cliff R.	NR145	41
	Kuwabara, James S.	WR190	73
	Lovley, Derek R.	NR123	37
	Luoma, Samuel N.	WR125	54

TOPIC	PROJECT CHIEF	PROJECT NUMBER	PAGE NUMBER
	McKnight, Diane M.	CR286	8
	Meade, Robert H., Jr.	CR309	91
	Nordstrom, Darrell K.	CR326	120
	Oremland, Ronald S.	WR174	67
	Seeley, James L.	CR316	289
	Simon, Nancy S.	NR135	303
	Stallard, Robert F.	CR313	98
	Taylor, Howard E.	CR282	276
	White, Arthur F.	WR196	178
Microbioloby			
Aerobic:	Oremland, Ronald S.	WR174	67
Anaerobic:	Godsy, Edward M.	WR068	52
	Harvey, Ronald W.	CR327	27
	Lovley, Derek R.	NR123	37
	Oremland, Ronald S.	WR174	67
	Smith, Richard L.	CR295	15
Models Statistical Methods:	Alley, William M.	NR148	349
	Cooley, Richard L.	CR191	193
	Landwehr, Jurate M.	NR133	342
	Moss, Marshall E.	WR201	373
	Naff, Richard L.	CR319	204
	Tasker, Gary D.	NR125	339
	Troutman, Brent M.	CR279	319
	Wagner, Brian J.	WR178	237
Nutrients:	Averett, Robert C.	CR312	19
	Bricker, Owen P.	NR109	300
	Callender, Edward	NR065	291
	Feder, Gerald L.	NR132	151
	LaBaugh, James W.	CR293	13
	Meade, Robert H., Jr.	CR309	91
	Peterson, David H.	WR046	48
	Smith, Richard L.	CR295	15
	Taylor, Howard E.	CR282	276
	Triska, Frank J.	WR186	70

TOPIC	PROJECT CHIEF	PROJECT NUMBER	PAGE NUMBER
Organic Compounds (natural):	Leenheer, Jerry A.	CR285	284
	Malcolm, Ronald L.	CR046	256
	McKnight, Diane M.	CR286	8
	Meade, Robert H., Jr.	CR309	91
	Wershaw, Robert L.	CR132	260
Organic Compounds (man-made):	Baedecker, Mary Jo	NR129	148
	Chiou, Cary T.	CR283	113
	Eganhouse, Robert P.	NR151	155
	Essaid, Hedeff I.	WR199	252
	Feder, Gerald L.	NR132	151
	Godsy, Edward M.	WR068	52
	Goerlitz, Donald F.	WR189	175
	Goldberg, Marvin C.	CR199	269
	Herkelrath, William N.	WR179	239
	Leenheer, Jerry A.	CR285	284
	Meade, Robert H., Jr.	CR309	91
	Pereira, Wilfred E.	WR204	309
	Rathbun, Ronald E.	WR301	323
	Wershaw, Robert L.	WR132	260
Radionuclides:	Cleveland, Jesse M.	CR223	108
	Davis, James A., III	WR065	159
	Kraemer, Thomas F.	NR138	153
	Landa, Edward R.	NR092	294
	Nordstrom, Darrell K.	CR326	120
Resevoirs:	Andrews, Edmund D.	CR273	87
	Averett, Robert C.	CR312	19
	Callender, Edward	NR065	291
	LaBaugh, James W.	CR293	13
	Marzolf, G. Richard	CR325	25
Sediment Chemistry:	Benson, Larry V.	CR207	273
	Callender, Edward	NR065	291
	Davis, James A., III	WR065	98
	Goldberg, Marvin C.	CR199	269
	James, Ronald V.	WR036	157
	Leenheer, Jerry A.	CR285	284

TOPIC	PROJECT CHIEF	PROJECT NUMBER	PAGE NUMBER
	Meade, Robert H., Jr.	CR309	91
	Stallard, Robert, F.	CR313	98
	White, Arthur F.	WR196	178
Sediment Transport:	Andrews, Edmund D.	CR273	87
	Bennett, James P.	WR197	371
	Chen, Cheng-lung	WR194	368
	Emmett, William W.	CR187	84
	Hupp, Cliff R.	NR145	41
	Meade, Robert H.	CR102	80
	Meade, Robert H., Jr.	CR309	91
	Osterkamp, Waite R.	CR311	94
	Smith, J. Dungan	CR324	101
	Stallard, Robert F.	CR313	98
	Webb, Robert H.	WR200	104
	Williams, Garnett P.	CR105	82
Snow, Ice, Glaciers:	Campbell, William J.	WR064	352
	Claassen, Hans C.	CR189	267
	Leavesley, George H.	CR228	314
	Reddy, Michael M.	CR284	280
	Walters, Roy A.	WR183	362
Surface Chemistry:	Davis, James A., III	WR065	159
	Eberl, Dennis D.	CR276	110
	Goldberg, Marvin C.	CR199	269
	Plummer, L. Niel	NR056	133
	Reddy, Michael M.	CR284	280
	White, Arthur F.	WR196	178
Surface-water Hydraulics:	Baltzer, Robert A.	NR019	328
	Bennett, James P.	WR197	371
	Chen, Cheng-lung	WR194	368
	Cheng, Ralph T.	WR140	357
	Jarrett, Robert D.	CR321	326
	Lai, Vincent C.	NR096	332
	Lee, Jonathan	NR147	347
	Schaffranek, Raymond W.	NR104	553
	Walters, Roy A.	WR183	362

TOPIC	PROJECT CHIEF	PROJECT NUMBER	PAGE NUMBER
Surface-water Transport and Reactions:	Bencala, Kenneth E.	WR187	364
	Cheng, Ralph T.	WR140	357
	Leavesley, George H.	CR228	314
	Rathbun, Ronald E.	CR301	323
	Triska, Frank J.	WR186	70
	Walters, Roy A.	WR183	362
Unsaturated Zone:	Chiou, Cary T.	CR283	113
	Claassen, Hans C.	CR189	267
	Constantz, James E.	WR193	248
	Essaid, Hedeff I.	WR199	252
	Herkelrath, William N.	WR179	239
	James, Ronald V.	WR036	157
	Milly, P.C.D.	NR144	345
	Nimmo, John R.	WR198	250
	Rubin, Jacob	WR180	242
	Stonestrom, David A.	WR024	224
	Thorstenson, Donald C.	NR093	143
	Weeks, Edwin P.	CR200	196
Wetlands:	Averett, R.C./Winter, T.C.	CR323	23
	Carter, Virginia P.	NR090	33
	Hupp, Cliff R.	NR145	41
	LaBaugh, James W.	CR293	19