Friedman, L.C.

NATIONAL RESEARCH PROGRAM OF THE WATER RESOURCES DIVISION, U.S. GEOLOGICAL SURVEY, FISCAL YEAR 1988

U.S. Geological Survey
Open-File Report 89-250

NATIONAL RESEARCH PROGRAM OF THE WRD, U.S. GEOLOGICAL SURVEY, FY 1988

NATIONAL RESEARCH PROGRAM

OF THE

WATER RESOURCES DIVISION,

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Compiled by
Linda C. Friedman and Christine N. Donato

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DEPARTMENT OF THE INTERIOR

MANUEL LUJAN, JR., Secretary

U.S. GEOLOGICAL SURVEY

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

FISCAL YEAR 1988

INTRODUCTION

The National Research Program (NRP) of the U.S. Geological Survey's Water Resources Division (WRD) had its beginnings in the late 1950's when "core research" was added as a line item to the Congressional budget. Since that time, 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. The knowledge gained and methods developed have great value to WRD's operational program. Results of the investigations conducted by the NRP are applicable not only to the solution of current water problems, but also to future issues, anticipated or unanticipated, that may affect the Nation's water resources.

The NRP is located principally in Reston, Va., Denver, Colo., and Menlo Park, Calif. 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. For technical administration, the NRP is subdivided into six disciplines with a Research Adviser assigned to each. The Research Adviser serves as a peer resource to the research projects and as a technical consultant to management. The six research disciplines are listed below along with the scope of their activity and current study emphasis:

(1) ECOLOGY--Studies biological and microbiological processes that affect solute composition and solute transport in surface and subsurface waters, and investigates the response of organisms, singly or in associations, to environmental factors to improve understanding of the biological effects of stress, hydrologic events, or climatic trends. 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 vary from ground waters to lakes, rivers and estuaries, and from coastal wetlands to forests and deserts.

(2) GEOMORPHOLOGY AND SEDIMENT TRANSPORT--Focuses on understanding fluvial processes that govern the source, mobility, and deposition of sediment in surface waters. Currently (1988), 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--Investigates inorganic, organic, and biochemical reactions affecting water quality in relation to mineralogical, 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 characteristics 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 investigate controls of mineral-water-gas reactions in a wide variety of hydrochemical environments, including regional aquifer systems, deep sedimentary basins and subsurface brines, geothermal systems, freshwater-saltwater interfaces, and the unsaturated zone. Studies include investigation of the degradation of organic matter and attenuation of toxic metals in environmentally stressed hydrochemical environments, a search for relations between water quality and human health and disease, and studies of 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 waters, predicting the thermodynamic properties of mineral-water reactions in brines and other highly saline fluids, and predicting chemical and isotopic evolution in water/rock systems.

(4) GROUND-WATER HYDROLOGY--Develops techniques that aid Federal, State and local agencies in evaluating, understanding, and managing ground-water resources. Research into the role of the unsaturated zone is being conducted to provide information needed to evaluate the feasibility of ground-water conservation and management tasks, such as artificial ground-water recharge, phreatophyte control, and the reduction of evapotranspiration loss. Currently (1988), 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, and 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 impact of acid rain on water quality.

(6) SURFACE-WATER HYDROLOGY--Stresses studies to improve the ability to predict the occurrence, distribution, movement, and quality 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 five areas: studies of (1) all hydrologic processes that govern the infiltration, evapotranspiration and runoff from basins, especially as they relate to an analysis of the effect of land use practices, such as surface mining, agriculture, and urbanization; (2) 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, and the areal distribution of hydrologic information, or the accuracy and reliability of deterministic models of hydrologic systems; (3) the hydraulics or hydrodynamics of flow in single or multidimensional surface-water systems and how this flow is related to the safety and welfare of man as he encroaches on the water body; (4) the sources, transport, and fate of constituents that are related to water quality in surface waters; and (5) the accumulation, movement, and melting of snow or ice, particularly the ways in which its presence affects climate, water supply, and/or safety.

This report provides current information about the NRP on an annual basis. Organized by the six research disciplines, the volume contains a summary of the problem, objective, approach, and progress for each project that was active during fiscal year 1988. Bibliographic information is included with each project summary in the form of reports published between April 1987 and May 1988.

The projects headquartered in each WRD Region are listed in Appendix I, which also lists the project number (five digits consisting of the appropriate two-letter WRD Region abbreviation followed by a three-digit sequencing number), the project short title, and the page number of the project summary. Appendix II is an alphabetic list of the Project Chiefs of all projects included in this volume along with the project short title, project number, and page number of the project summary.

This publication is intended for use primarily by the U.S. Geological Survey in program development, coordination, and review. Some of the project summaries may include tentative results that need further study and testing before they are verified. The publication is distributed to members of the Survey staff and the general public that have a special interest in water-resources research.

ECOLOGY

CR286 ORGANIC-TRACE METAL INTERACTIONS

TITLE: Interactions Between Organic Solutes and Trace Metals in Natural Waters, and Their Ecological Role

PROJECT NUMBER: CR 84-286

LOCATION: Topical Research

PROJECT CHIEF: McKnight, Diane M.

HEADQUARTERS OFFICE: Arvada, CO

PROBLEM: Aquatic humic substances and other classes of dissolved organic material present in natural waters can control the biogeochemistry of many important trace metals. These include trace metals that are (1) involved in weathering reactions, (2) important micronutrients, and (3) possible toxicants at natural or elevated concentrations. Recent advances in organic geochemistry can be used to determine the importance of interactions between organic solutes and trace metals in aquatic environments. Metal-binding sites of humic substances probably are composed of carboxylic-acid groups, but the exact chemical structure and mechanisms are not known. These data are critical to understanding the dependence of metal binding on pH, and concentration of major cations, such as calcium, magnesium, and sodium. Another unknown is the metal-binding properties of nonhumic organic solutes in natural waters, especially those associated with the growth and decomposition of aquatic microorganisms.

OBJECTIVE: (1) Isolate and characterize aquatic humic substances and other organic acids from several aquatic environments; (2) determine the dependence of trace-metal binding by humic substances on the nature and concentration of counter ions (H^+, Ca^{2+}, Mg^{2+}, Na^+) and use these results to develop a polyelectrolyte model for humic substances; (3) determine the processes that control the biogeochemistry of dissolved organic material and selected trace metals in several aquatic environments; and (4) characterize the uptake of iron and copper by freshwater algae as controlled by complexation by aquatic humic substances.

APPROACH: (1) Isolate and characterize aquatic humic substances and other organic acids from several current field sites using conventional methods; (2) conduct potentiometric titrations and other laboratory experiments to determine the dependence of copper and iron complexation by humic substances on pH and counter-ion concentration; (3) continue ongoing field studies of biogeochemical interactions between dissolved organic material and trace metals. Field sites include a mountain stream system, several alpine lakes, and a bog.

PROGRESS: Under a National Science Foundation grant, a field study of algal-derived dissolved organic carbon (DOC) in Antarctic desert lakes was successfully conducted during the austral summer. Initial analyses show that the algal-derived humic substances are very similar in composition to marine humic substances, and may indicate that the main DOC flux is diffusive transport of DOC produced by anaerobic degradation of algal material in the lake sediments. Six months of data were collected for a study of the annual trace metal budget in an ombrotrophic bog; these data will be integrated with DOC data and used to evaluate the importance of trace metal-organic interactions in such wetlands. A final paper describing the diagenetic changes in dissolved humic substances in Spirit Lake in the blast zone of Mt. St. Helens has been accepted for publication and a paper on photoreduction and oxidation of iron in a stream that is being studied as part of the Surface Water Toxics Program was published in Science.

REPORTS PUBLISHED:

McKnight, D. M., and Feder, G. L., in press, Ecological aspects of humic substances in the environment, in MacCarthy, P., and others, eds., Humic Substances: Environmental Interactions: London, John Wiley.

McKnight, D. M., Kimball, B. A., and Bencala, K. E., 1988, Iron photoreduction and oxidation in an acidic mountain stream: Science, v. 240, p. 637-640.

Averett, R. C., and McKnight, D. M., eds., 1987, Chemical quality of water and the hydrologic cycle: Proceedings of the 8th Rocky Mountain Regional Meeting of the American Chemical Society, Chelsea, Mich., Lewis Publishers, Inc.

Bencala, K. E., and McKnight, D. M., 1987, Identifying in-stream variability: sampling iron in an acidic stream, in Averett, R. C., and McKnight, D. M., eds., Chemical quality of water and the hydrologic cycle: Chelsea, Mich., Lewis Publishers, p. 255-270.

CR293 HYDROL-BIOL GEOCHEM INTERACTIONS

TITLE: The Role of Chemical Fluxes in the Biogeochemistry of Inland Surface Waters, Including Lakes, Reservoirs, and Wetlands

PROJECT NUMBER: CR 85-293

LOCATION: Topical Research

PROJECT CHIEF: LaBaugh, James W.

HEADQUARTERS OFFICE: Lakewood, CO

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

OBJECTIVE: Determine the mechanisms controlling fluxes of biologically important chemical elements between surface waters and their watersheds. Examine the different transport pathways that affect the supply and loss of those elements from surface waters and use empirical and conceptual models of hydrological-biological interactions to identify mechanisms to be investigated further in the field.

APPROACH: Determine the mechanisms controlling supply and loss of biologically important chemical elements in surface waters (lakes, reservoirs, and wetlands) using data from new field work and using previously collected data from intensively studied field sites. Use field data to develop empirical and conceptual models that, in turn, will suggest areas of further field research into hydrological-biogeochemical interactions.

PROGRESS: One professional paper was published. A journal article report relating hydrogeologic setting to chemical characteristics of lakes and wetlands at three field sites was published. A paper on the algae and invertebrates found in the water columns of selected seasonal and semipermanent wetlands of the Cottonwood Lake area (North Dakota) was prepared and is in review. A paper was written about the chemical characteristics of ground water in the watershed of Mirror Lake, N.H., and is in review. Intensive studies of chemical fluxes, including determination of ground-water flux, and in-lake chemical and biological investigations continued at Cottonwood Lake wetlands, N. Dak., Cresent Lake refuge, Nebr., and Williams Lake, Minn.

WRD FEDERAL RESEARCH PROJECTS.....ECOLOGY

REPORTS PUBLISHED:

LaBaugh, J. W., in press, Chemical characteristics of water in northern prairie wetlands, in van der Valk, A. G., ed., Northern prairie wetlands: Ames, Iowa, Iowa State University Press, ch. 3.

Winter, T. C., LaBaugh, J. W., and Rosenberry, D. O., in press, The design and use of a hydraulic potentiomanometer for direct measurement of differences in hydraulic head between ground water and surface water: Limnology and Oceanography, v. 33, no. 4.

LaBaugh, J. W., Winter, T. C., Adomaitis, V. A., and Swanson, G. A., 1987, Hydrology and chemistry of selected prairie wetlands in the Cottonwood Lake area, Stutsman County, North Dakota 1979-82: U.S. Geological Survey Professional Paper 1431, 26 p.

LaBaugh, J. W., 1988, Relation of hydrogeologic setting to chemical characteristics of selected lakes and wetlands within a climate gradient in the North Central United States: Verhandlungen Internationale Vereinigung Limnologie, v. 23, p. 131-137.

CR295 MICROBIAL GEOCHEM OF ORGANIC MATTER

TITLE: Microbial Transformation of Dissolved Organic Carbon in Aquatic Environments

PROJECT NUMBER: CR 86-295

LOCATION: Topical Research

PROJECT CHIEF: Smith, Richard L.

HEADQUARTERS OFFICE: Arvada, CO

PROBLEM: Although it is recognized that microorganisms play an important role in the transformation of organic compounds in aquatic habitats, very little is known about the exact nature of these processes. This is true for pristine and contaminated environments. Within the context of in situ environmental conditions, the mechanisms, pathways, rates, and factors controlling carbon cycling by microorganisms are poorly understood. However, these 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 (both naturally occurring and contaminant) mediated by micro-organisms in aquatic habitats and identify some of the factors controlling these processes. Examine the effect that these transformations have upon other biogeochemical processes.

APPROACH: Select a pristine alpine stream and a sewage-contaminated ground-water aquifer as the habitats for primary focus. Determine microbial processes in both water and sediment samples using tracer techniques for both laboratory and field studies. Develop sample-handling techniques needed to maintain in situ conditions. When necessary, experiments with isolated cultures of micro-organisms will be employed to help interpret the results obtained with natural samples.

PROGRESS: Research efforts were focused upon carbon and nitrogen cycling in ground water at the Cape Cod Hazardous Waste Site in Massachusetts and in a permanently stratified lake, Lake Fryxell, in Antarctica. (1) Using injected tracers at the Cape Cod site, methane oxidation by microorganisms in the subsurface was demonstrated in situ. This activity occurred in both an aerobic, pristine section of a sand and gravel aquifer and in a contaminated anoxic portion of the same aquifer. In the latter case, methane oxidation occurred in a zone in which denitrification was the predominant terminal electron accepting process. This is the first time that methane oxidation and denitrification have been shown to co-occur in aquatic samples, and suggests a new, previously unknown, microbial process. (2) Supported by a National Science Foundation Grant, carbon cycling in Lake Fryxell in the

Taylor Dry Valleys in Antarctica was studied. The lakes in this area are permanently stratified and sealed from exchange with the atmosphere by a permanent ice cover. In addition, the lakes contain no higher plants in their watersheds. The stable stratification in the water column of Lake Fryxell enabled a correlation of the chemical nature of the dissolved organic carbon within the distinct zones in the water column with the specific microbial processes within each zone. The water column contained an oligotrophic zone of low productivity, a hyperoxic layer of primary productivity, and a deep, sulfide-rich, anoxic zone. These zones were reflected in both the inorganic and organic geochemistry of the lake.

REPORTS PUBLISHED:

Smith, R. L., and Oremland, R. S., 1987, Bacterial activities in the water column of Big Soda Lake. II. Sulfate reduction: Limnology and Oceanography, v. 32, p. 794-803.

Smith, R. L., and Duff, J. H., 1988, Denitrification in contaminated ground water: Applied and Environmental Microbiology, v. 54(5), p. 1071-1078.

Ceazan, M. L., 1987, Migration and transformation of ammonium and nitrate in a sewage-contaminated aquifer at Cape Cod, Mass.: M.S. Thesis, Colorado School of Mines.

CR312 ECOLOGY OF LAKES AND STREAMS

TITLE: Ecological Interactions of Lakes and Streams

PROJECT NUMBER: CR 88-312

LOCATION: Topical Research

PROJECT CHIEF: Averett, Robert C.

HEADQUARTERS OFFICE: Arvada, CO

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

APPROACH: Select several stream sites above lakes and the receiving lakes, instrument for flow and temperature, and map for geomorphic features. Measure number and type of aquatic flora and fauna. Determine the effect that alterations in the hydrologic regime, including geomorphic changes, have upon stream and lake organisms determined.

PROGRESS: Project field sites in Wyoming and possible sites in New York are being selected. Site selection for streams to be included in the Rocky Mountain Chemical Study are underway. A memorandum to all field offices was sent in an effort to find several lakes for intensive study for the Integrated Aquatic-terrestrial Ecosystem study. Some 84 replys were received and a selection of two or more lakes is being made.

REPORTS PUBLISHED:

Averett, R. C., 1988, Major factors affecting pollutant export and unit area loads to receiving waters: UNESCO publication on non-point source pollution, 24 p.

Averett, R. C., and Marzolf, G. R., 1987, Water Quality: Environmental Science and Technology, v. 21, no. 9, p. 827.

NR027 PLANT GROWTH AND HYDROLOGY

TITLE: Basic Research Concerning Periodic Plant Growth Phenomena and Hydrology

PROJECT NUMBER: NR 66-027

LOCATION: Topical Research

PROJECT CHIEF: Phipps, Richard L.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: Many plant growth phenomena are controlled in part by environmental conditions. Because water availability to plants seems to be the single most important factor limiting physiological processes in plants, relations must exist between hydrologic factors or conditions and various plant-growth phenomena. Studies to date indicate that such relations are complex and little understood. Such an understanding must be established before plants can be fully utilized to interpret hydrologic phenomena.

OBJECTIVE: Basic research objectives include the determination of relation between characteristics of the hydrologic environment and periodic plant-growth phenomena. The ultimate objective is to use data from interannual and intra-annual tree-growth parameters (tree rings) to estimate or reconstruct, on a temporal or spatial basis, parameters of the hydrologic environment. A specific long-range objective is to determine relationships between tree growth and environmental pollutants (including heavy metals as well as atmospheric pollutants). Short-range objectives are intended to contribute toward long-range objectives through methods development and establishment of a data base.

APPROACH: Collect data of growth responses of many species in innumerable habitats to ascertain types of information regarding hydrologic environment recorded in plant growth. Prepare a data base composed primarily of measured annual increments of radial growth of trees, and include other parameters of growth, such as wood anatomy and various ecological and mensuration statistics. The basic approach is to (1) identify a specific problem, examine the botanical growth processes involved, (2) describe the relationships between these processes and the aspect of the hydrologic environment under consideration, and (3) use botanical evidence to interpret, estimate, or extend records of the hydrologic environment.

PROGRESS: Element-analysis of trees growing on a polluted site in the Aberdeen Proving Ground in Maryland demonstrated that element content of individual rings is variable among trees, along different parts of a single ring, and appears unrelated to ring width. Year-to-year trends of element content of wood samples support hypotheses of the past movement of pollutants in the shallow ground-water system. Examination of time trends in basal area increments of 60 tree-ring collections of white oak from throughout eastern United States has identified a growth decline that began in the 1950's. The decline appears as a simple decrease in growth rate unrelated to air pollution, climate, geographic location, site quality, or the oak "decline" commonly noted in red oak species. No explanation for the decline has been proposed.

NR090 WETLAND STUDIES

TITLE: Remote Sensing and Ecological Research in Wetlands

PROJECT NUMBER: NR 73-090

LOCATION: Topical Research

PROJECT CHIEF: Carter, Virginia P.

HEADQUARTERS OFFICE: Reston, VA

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 (oxygen) stress; water-quality characteristics such as salinity, turbidity, pH, nutrients; presence of various pollutants; or frequency and duration of inundation. Submersed aquatic vegetation has many functional values 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 nutrients and heavy metals. Decline or disappearance of aquatic plant communities is of concern to scientists, ecologists, environmentalists, and managers. Overgrowth of submersed vegetation under nutrient-enriched conditions also is a problem. The processes affecting distribution and abundance and the factors contributing to the balance between phytoplankton and macrophytes are understood poorly.

OBJECTIVE: (1) Characterize wetland-transition zones and relate distribution of vegetation in Dismal Swamp in Virginia and North Carolina to soils, hydrology, and elevation; (2) examine seasonal and long-term changes in wetland ecology as related to changes in environmental parameters including hydrology, water quality, and land use; (3) aid in the development of models that use remote sensing or biological hydrologic data as part of their primary data base; (4) determine factors responsible for the changing distribution of aquatic beds and the resurgence of submersed macrophytes in the tidal Potomac River; (5) monitor the spread of Hydrilla and competition with other macrophytes; and (6) consider processes affecting flux of materials from vegetation to soil or water column or vice versa.

APPROACH: (1) Measure ground-water levels, surface-water inundation, ground and soil O_2, and recharge and discharge relation on the western transition zone of Dismal Swamp; (2) collect data on ground and surface water in major vegetation communities as well as data on elevation, depth of organic soil, water table, and surface flooding; (3) conduct field and laboratory

investigations of the survival of submersed aquatic plants under a variety of conditions and in different locations; (4) conduct yearly field surveys to document distribution, abundance, and species composition, and (5) develop models illustrating relation between plant success and other environmental factors.

PROGRESS: During 1987, submersed aquatic macrophytes continued to spread downstream in the tidal Potomac River. Populations remained small and patchily distributed in the lower tidal river where light penetration is low. The large beds of vegetation in the upper tidal river were found to improve water clarity in the beds, to increase the uptake of sediment nutrients, to raise the dissolved oxygen concentrations and pH in the beds and adjacent water during the day, and to reduce phytoplankton populations in the beds. Results from studies in 1978-85 in the Great Dismal Swamp of Virginia and North Carolina are being published. Publications include information on the relation of soils, hydrology, and vegetation on the wetland-to-upland transition zone, oxygen dynamics in the transition zone, and boundary determination in forested wetlands.

REPORTS PUBLISHED:

Carter, Virginia, Rybicki, N. B., and Schulman, C. L., 1987, Effect of temperature and salinity on germination of monoecious hydrilla propagules: Journal of Aquatic Plant Management, v. 25, p 54-57.

Carter, Virginia, Garrett, M. K., and Gammon, P. T., 1988, Wetland boundary determination in the Great Dismal Swamp using weighted averages: Water Resources Bulletin, v. 24, no. 24, p. 297-306.

Rybicki, N. B., Anderson, R. T., Shapiro, J. M., Johnson, K. L., and Schulman, C. L., 1987, Data on the distribution and abundance of submersed aquatic vegetation in the tidal Potomac River and Estuary, Maryland, Virginia, and the District of Columbia, 1986: U.S. Geological Survey Open-File Report 87-575, 82 p.

Rybicki, N. B., Anderson, R. T., And Carter, Virginia, in press, Data in distribution and abundance of submersed aquatic vegetation in the tidal Potomac River and transition zone of the Potomac Estuary, Maryland, Virginia and the District of Columbia, 1987: U.S. Geological Survey Open-File Report 88-307, 47 p.

NR136 MICROBIAL GEOCHEMICAL MODELS

TITLE: Modelling of Microbially-Catalyzed Geochemical Reactions in Aquatic Environments

PROJECT NUMBER: NR 87-136

LOCATION: Topical Research

PROJECT CHIEF: Lovley, Derek R.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: Microorganisms 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 microorganisms that control the rate and extent of microbially-catalyzed reactions.

OBJECTIVE: (1) Quantify the rates of microbial process that influence the geochemistry of surface- and ground-water aquifers; (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- and ground-water aquifers.

APPROACH: Rates and pathways of microbial processes will be quantified with radiotracer, stable isotope and inhibitor techniques. Microbial physiological characteristics will be determined with experimental manipulations of natural mixed populations and pure cultures. Data on physiological characteristics will be combined with appropriate geochemical models to generate models for the distribution of microbial processes.

PROGRESS: Basic aspects of the physiology of a unique iron- and manganese-reducing micro-organism were characterized. This organism was found to be the first one known to be able to completely oxidize organic compounds with iron or manganese as the sole electron acceptor. Organisms with a similar metabolism were cultured from deep subsurface sediments. The metabolism of these organisms provides the first microbiological mechanism for the reduction and solubilization of significant quantities of iron and manganese in aquatic environments. A theoretical model based on the physiology of anaerobic, hydrogen-consuming organisms was developed which explains previous observations that sediments with the same terminal electron-accepting processes have similar hydrogen concentrations and that hydrogen concentrations are lower in sediments with more electrochemically positive terminal electron acceptors. Hydrogen oxidation coupled to the reduction of iron or manganese was shown to be an enzymatically catalyzed reaction in sediments and a microorganism capable of coupling hydrogen oxidation to the reduction of iron or manganese was discovered. Hydrogen concentrations in aquifers in Maryland and South Carolina

and in sediments of hypersaline Mono Lake, Calif., were studied. These studies have advanced attempts to develop the use of hydrogen gas as an indicator of the predominant microbially catalyzed redox reactions taking place in surface and deep subsurface sedimentary environments. Mechanisms for the inhibition of microbial iron reduction in the presence of manganic oxides were elucidated. The abiotic oxidation of ferrous iron by manganic oxides, rather than preferential reduction of manganic oxides by iron-reducing bacteria, was found to be the most important factor preventing the accumulation of ferrous iron in sediments containing manganic oxides. These results add another component to the developing model for the mechanisms controlling the distribution of anaerobic microbial processes in sediments. Studies on the factors limiting the rate of organic matter decomposition in subsurface aquifers were initiated in cooperation with the South Carolina district. Preliminary results suggest that the major factor limiting microbial metabolism is the availability of the appropriate electron acceptors.

REPORTS PUBLISHED:

Lovley, D. R., and Phillips, E. J. P., 1987, Rapid assay for microbially reducible ferric iron in aquatic sediments: Applied and Environmental Microbiology, v. 53, p. 1536-1540.

Phillips, E. J. P., and Lovley, D. R., 1987, Determination of Fe(III) and Fe(II) in oxalate extracts of sediment: Soil Science Society of America Journal, v. 51, p. 938-941.

Lovley, D. R., and Phillips, E. J. P., 1987, Competitive mechanisms for inhibition of sulfate reduction and methane production in the zone of ferric iron reduction in sediments: Applied and Environmental Microbiology, v. 53, p. 2636-2641.

Lovley, D. R., 1987, Organic matter mineralization with the reduction of ferric iron: A review: Geomicrobiology Journal, v. 5, p. 375-399.

Lovley, D. R., Stolz, J. F., Nord, G. L., Jr., and Phillips, E. J. P., 1987, Anaerobic production of magnetite by a dissimilatory iron-reducing microorganism: Nature, v. 330, p. 252-254.

Lovley, D. R., and Phillips, E. J. P., in press, Novel mode of microbial energy metabolism: Organic carbon oxidation coupled to dissimilatory reduction of iron or manganese: Applied and Environmental Microbiology, v. 54.

WR012 LIMNOLOGY: BENTHIC COMMUNITIES

TITLE: Limnology: Controls on Distribution and Composition of Benthic Communities of Inland Aquatic Ecosystems

PROJECT NUMBER: WR 61-012

LOCATION: Topical Research

PROJECT CHIEF: Slack, Keith V.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Benthic invertebrates are the aquatic organisms most widely used as indicators of environmental quality in streams. Although many factors are known to affect the abundance and distribution of species, it is usually not possible to predict expected changes in benthic communities for a given impact. 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. The ability to predict such changes awaits greater knowledge of the functional relations between benthic invertebrates and other components of stream ecosystems.

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 stream biotic communities.

APPROACH: In a variety of small to large streams, sample benthic invertebrates and relate their spatial and temporal distribution and species composition to environmental differences using multivariate analysis. Test relationships derived from field studies in field and laboratory experiments.

PROGRESS: Nested nets of different porosity were used to study mesh-size effects on collection of invertebrate drift. The innermost, middle, and outermost nets had, respectively, 425 um, 209 um and 106 um mesh openings, an arrangement that decreased clogging while partitioning collections into three size groups. The open area of mesh in each net, from largest to smallest mesh opening, was 3.7, 5.7, and 8.0 times the area of the net mouth. Volumes filtered were determined with a flowmeter. During low flow in Deer Creek, Colo., the 425 um mesh retained the largest volume of sediment and detritus and the 209 um mesh retained the smallest volume. The insect family Chironomidae was numerically dominant in all 209 um and 106 um collections and in midday 425 um collections. Large mayfly and stonefly nymphs occurred only in 425 um or 209 um nets, but the general pattern was an increase in abundance and number of species with decreasing mesh size. The influence of mesh size on the composition of drift collections was not uniform over the

diel cycle, and relatively more of the total individuals occurred in nets with the larger mesh openings at night than during the day. This is consistent with previous studies showing generally larger drifting invertebrates at night than during the day.

REPORTS PUBLISHED:

Slack, K. V., Tilley, L. J., and Hahn, S. S., in press, Collection of benthic invertebrates by drift net and dip net, Little Boulder Creek, Idaho, in Selected Papers in the Hydrologic Sciences: U.S. Geological Survey Water-Supply Paper 2330.

WR046 GEOCHEM RIVERS AND ESTUARIES

TITLE: Geochemistry of Riverine and Estuarine Waters

PROJECT NUMBER: WR 68-046

LOCATION: San Francisco Bay, CA

PROJECT CHIEF: Peterson, David H.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Physical and chemical processes and rates (PAR) that control changes in water and sediment chemistry in river, estuary, and coastal-ocean systems are defined poorly. An understanding of PAR is essential to assess the response of these systems to variations in climate and human activities that can lead to changes in the amount, character, and timing of freshwater, toxic waste, sediment, and plant-nutrient inflows to these environments.

OBJECTIVE: Define dominant PAR that influence and control water and sediment chemistry (primarily oxygen, carbon, silicon, nitrogen, and phosphorous) in riverine, estuarine, and coastal ocean environments, including partially mixed and stratified environments.

APPROACH: Identify and analyze vertical and horizontal PAR that control the supply, removal, and dilution of chemical substances in these environments by comprehensive field (shipboard and in situ instrumentation) and numerical simulation methods. As data become available, systems variability is analyzed on various scales; for example, interannual variability (primarily climate-related), long-term trends (human factors) as well as seasonal and short-term source-sink processes (photosynthesis/mineralization).

PROGRESS: In conjunction with research in Tomales Bay by S. Smith, University of Hawaii, advances have been made to our understanding of how to measure amorphous silica in sediment. In conjunction with the California District and the California Department of Water Resources, a benthic clam was discovered that is new to the San Francisco Bay estuary (heretofore found in estuaries of Asia). In cooperation with A. Vecchia, Colorado State University, it was shown that periodic, auto-regressive, moving-average models of streamflow can provide a very close approximation (with few parameters) to the annual pattern in auto correlation structure even for a variety of rivers and streams. Work with D. Cayan (Scripps Institution of Oceanography) showed important effects of the winter North Pacific large-scale atmospheric circulation patterns in western North America on large-scale anomalous streamflow patterns. Such results also appear to be linked to stream chemistry, to the extent that variations in stream chemistry are flow-related. Work with J. Festa (National Oceanic and Atmospheric Administration, Miami) showed that bulk optical properties (specific absorption and c:chl ratio) of phytoplankton are important in numerical simulation models and cause large variations in

ambient phytoplankton biomass. Extremes in simulation results appear to be qualitatively similar to extremes published in the open literature for real systems; for example, Chesapeake Bay, high biomass, high c:chl ratio, low specific absorption vs. Puget Sound, low biomass, perhaps low c:chl ratio and, apparently, higher specific absorption.

REPORTS PUBLISHED:

Peterson, D. H., Bencala, K. E., Perry, M. J., and Talbot, M. K., 1987, Phytoplankton productivity in relation to light intensity: a simple equation: Estuarine Coastal and Shelf Science, v. 24, p. 813-832.

Peterson, D. H., Hager, S. W., and Schemel, L. E., 1988, Riverine C, N. Si and P transport to the coastal ocean: an overview: Lecture Notes on Coastal and Estuarine Studies, v. 22, p. 227-253.

Peterson, D. H., Cayan, D. R., DiLeo-Stevens, J., and Ross, T. G., 1987, Some effects of climate variability on hydrology in western North America: Proceedings of the International Association of Hydrological Sciences, no. 168, p. 45-62.

Smith, S. V., Wiebe, W. J., Hollibaugh, J. T., Dollar, S. J., Hager, S. W., Cole, B. E., Tribble, G. W., and Wheeler, P. A., 1987, Stoichiometry of C, N, P, and Si fluxes in a temperate-climate embayment: Journal of Marine Research, v. 45, p. 427-460.

WR068 ORGANIC CHEMICALS IN SUBSURFACE

TITLE: Fate of Organic Chemicals in Subsurface Environments

PROJECT NUMBER: WR 71-068

LOCATION: Topical Research

PROJECT CHIEF: Godsy, Edward M.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Release of various synthetic organic compounds to the environment has caused soil and ground-water pollution in many places. The processes which control the persistence and movement of these materials 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 using 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; (3) study relevant biotransformation processes occurring 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 simulations studies to elucidate the controls on these transformations.

PROGRESS: The movement and fate of the major water soluble compounds in creosote are being studied, both in the laboratory and at the USGS Hazardous Waste Study Site at Pensacola, Fla. The anaerobic microbial degradation pathways for several of the major components of the water soluble fraction have been determined in laboratory digestors using high pressure liquid chromatography and gas chromatography-mass spectrometry techniques. Computer programs for the determination of kinetic microbial growth parameters from laboratory growth studies and the adsorption of organic compounds in laboratory columns have been developed. The kinetic parameters and sorption characteristics have been determined for several of the major water soluble compounds.

REPORTS PUBLISHED:

Godsy, E. M., Goerlitz, D. F., and Grbic'-Galic', Dunja, 1987, Anaerobic biodegradation of creosote contaminants in natural and simulated ground-water ecosystems, in Franks, B. J., ed., U.S. Geological Survey program on toxic waste--ground-water contamination: Proceedings of the third technical meeting, Pensacola, Fla., March 23-27, 1987: U.S. Geological Survey Open-File Report 87-109, p. A13-A19.

Godsy, E. M., Goerlitz, D. F., and Ehrlich, G. G., 1987, Effects of penta-chlorophenol on the methanogenic fermentation of phenol, in Ragone, S. E., and Sulam, D. J., eds., Program overview and selected papers from the Toxic-Waste Program technical meeting: Tucson, Arizona, March 20-22, 1984: U.S. Geological Survey Open-File Report 86-324, p. 101-106.

WR125 TRACE ELEMENTS AVAILABILITY IN SEDIMENTS

TITLE: Availability of Trace Elements in Sediments to Aquatic Organisms

PROJECT NUMBER: WR 75-125

LOCATION: Topical Research

PROJECT CHIEF: Luoma, Samuel N.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Concentrations of potentially toxic elements in sediments are orders of magnitude higher than concentrations 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 predicting assimilation capacities. Assessment of biological indicator data for mineral exploration and pollution assessment also depend upon understanding 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, at least partly, be 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 upon metal uptake and metal effects in organisms that contact sediments directly; (3) study physiological characteristics of aquatic organisms that uptake metal; (4) improve methodology which uses 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; statistically assess relation of metal concentrations in organisms to aspects of the specific geochemical gradient under study. (2) Use laboratory studies to assess the biological influences on metal burdens in animals, 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: Finished review papers on metal contamination in San Francisco Bay and on metal bioavailability from sediments. Finished papers on Trace Elements in Suisun Bay. Completed model analysis of biological processes that affect metal concentrations in bivalves; paper in progress. Developed model describing metal dispersing processes in sediments of Clark Fork River, Mont., and tributaries; paper in progress. Determined metal distributions in insects from unpolluted Clark Fork Tributary. Began experiment studying specific sediment changes that affect the bioavailability of silver. Began synthesis of data assessing uses of stream benthos as geochemical sentinel organisms.

REPORTS PUBLISHED:

Cain, D. J., Thompson, J. K., and Luoma, S. N., 1987, The effect of differential growth on spatial comparisons of copper content of a bivalve indicator, in Lindberg, S. E., and Hutchinson, T. C., eds., Heavy metals in the environment: Edinburgh, CEP Consultants Ltd., p. 455-458.

Axtmann, E. V., and Luoma, S. N., 1987, Trace metal distribution in floodplain and fine bed sediment of the Clark Fork River, MT, in Lindberg, S. E., and Hutchinson, T. C., eds., Heavy metals in the environment: Edinburgh, CEP Consultants Ltd., p. 494-498.

Johns, C., and Luoma, S. N., 1987, Accumulation of selenium in benthic bivalves and fine-grained sediments of San Francisco Bay, the Sacramento-San Joaquin Delta and selected tributaries, 1984-1986: U.S. Geological Survey Open-File Report 87-562, 57 p.

WR137 TOXIC SUBSTANCES: AQUATIC ECOSYSTEMS

TITLE: Effects of Toxic Substances on Aquatic Communities

PROJECT NUMBER: WR 75-137

LOCATION: Nationwide

PROJECT CHIEF: Leland, Harry V.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Ecological effects in surface waters of toxic materials are of concern. Standard methods for evaluating effects of toxic substances in aquatic ecosystems are not available. Several promising, but untested, methods are available to determine responses of individual species and are of potential value in monitoring programs. Data from field and laboratory ecosystems which show the effects of environmental concentrations of toxicants on the function and structure of aquatic communities are largely lacking.

OBJECTIVE: Determine through detailed studies of organisms, simplified ecosystems, and natural sites, the extent to which trace metals and stable organic compounds affect the production and structure of aquatic-plant assemblages and the growth and reproductive capacity of aquatic animals. Evaluate methods of assessing effects of chronic exposures of toxicants on individual species and natural aquatic communities.

APPROACH: Evaluate methods for assessing effects of toxic substances released to the environment. These include tests of embryogenesis and growth in fishes, specific birth rate and survival of critical life stages of aquatic invertebrates, and population growth rate of algae. Determine physico chemical factors affecting responses and bioaccumulation of these toxic substances. Examine trophic dynamics of simplified aquatic ecosystems (experimental streams) exposed to trace metals and stable organic compounds. Evaluate methods and results of laboratory and experimental stream studies by field experiments. Determine the utility of the biological test methods for detecting and monitoring environmental concentrations of toxicants. Examine the factors (physico chemical and biological) influencing responses of natural aquatic communities.

PROGRESS: Effects of agricultural return flows on aquatic communities of the San Joaquin River in California are being studied. Elevated concentrations of arsenic, selinium, mercury, and cadmium are present in soft tissues of Corbicula (asiatic clam) at sites impacted by subsurface irrigation wastewater. Concentrations of organochlorine insecticides in clams are highest at sites with a significant portion of their flow as surface runoff from agricultural land. Eichhornia (water hyacinth) is being evaluated for its potential as a biological monitor of metal contamination. Significant relationships between elemental concentrations in Eichhornia roots and dissolved concentrations in riverwater were observed for aluminum, manganese, sodium, and selinium. Indirect gradient ordination and canonical correlation are being used to elucidate species-environment relationships for periphyton and benthic invertebrates. The structures of these communities colonizing stable substrates are strongly related to concentrations of salts from agricultural return flows. Dissolved oxygen and nutrient (N and P) supply are also significant factors affecting structure of the invertebrate community, whereas nutrient supply and turbidity are additional factors affecting structure of the periphyton. Studies of species-environment relationships for benthic invertebrates in the Yakima River, Wash., were initiated by determining the spatial distributions of common taxa after prolonged periods of low flow in autumn and early spring.

REPORT PUBLISHED:

Cain, D. J., Fend, S. V., and Carter, J. L., 1987, Arsenic concentrations of selected benthic insects in Whitewood Creek and the Belle Fourche River, S. Dak., in Mallard, G. E., ed., U.S. Geological Survey Toxic Substances Hydrology Program - Surface-Water Contamination, Proceedings of the Technical Meeting, Denver, Colorado, 1987: U.S. Geological Survey Open-File Report 87-764.

Leland, H. V., Carter, J. L., Fend, S. V., and Jenkins, T. M., 1988, Effects of copper on structure and function of biological communities in a Sierra Nevada, California, stream: Aquatic Toxicology, v. 11, p. 409.

Scudder, B. C., Carter, J. L., and Leland, H. V., 1988, Effects of copper on development of the fathead minnow, Pimephales promelas Rafinesque: Aquatic Toxicology, v. 12, p. 107-124.

WR145 VEGETATION ECOHYDROLOGY

TITLE: Ecohydrology of Arid Region Vegetation

PROJECT NUMBER: WR 76-145

LOCATION: Arizona, arid regions

PROJECT CHIEF: Turner, Raymond M.

HEADQUARTERS OFFICE: Tucson, AZ

PROBLEM: Water is becoming increasingly scarce in the arid region of the United States. In their attempt to manage or control this essential resource, humans constantly modify regional hydrology by changing watertable elevations, altering surface-drainage patterns, controlling streamflow, and altering erosion. These and other modifications may result in altered water quality and often result indirectly in vegetation changes that reflect the changed regional hydrology. Humans also change the vegetation directly through agricultural practices, urbanization, and vegetation management activities, all of which have an impact on the region's hydrology.

OBJECTIVE: Define the interrelation between the region's hydrology and its vegetation. Measure the effect that the changing patterns of vegetation have on the regional water supply, and conversely, the effect that changes in water quality and quantity have on the vegetation.

APPROACH: Use historical documents and old photographs to determine the scope of vegetation changes over time. Use remote sensing products such as aerial photographs and satellite images to locate, map, and measure existing vegetation. Riparian and phreatic vegetation will be emphasized because, compared to the area they occupy, their hydrologic and ecological significance is disproportionately great. The communities are valuable wildlife habitats and recreation sites; at the same time, they consume and transpire large amounts of water. Studies of desert plant populations will be made because vegetation changes at dry sites may be sensitive indicators of large-scale climatic change.

PROGRESS: Analysis of monthly precipitation showed that climatic variability in the Southwest is related to the mean meridional circulation and the relative strength and frequency of El Nino-Southern Oscillation (ENSO) events. The periods 1900-1930 and 1960-1988 experienced meridional circulation, frequent ENSO events, wet conditions in the cool half-year, and reduced intensity of the summer monsoons. A more zonal circulation and infrequent ENSO activity during 1930-1960 produced drought over much of the Southwest. These climatic trends were identified in annual flood series, forest-fire chronologies, and population fluctuations of long-lived desert plants. Climatic variability was identified as a source of nonstationarity in flood series from southern Arizona streams. Inspection of fire-scar chronologies

from ponderosa pine showed that 80 percent of ENSO events during the past 300 years were associated with low fire activity. This probably is due to wetter foresummers and reduced lightning intensity in midsummer. The record from southwestern packrat middens demonstrated that ponderosa pine forests were more unstable than might have been anticipated from their current dominance. Given fire supression, which reduces recruitment in ponderosa pine, and its natural susceptibility to climatic variability, forests in the headwaters of the Rio Grande and Colorado River basins are unlikely to remain stable with future climatic change. Quantitative paleotemperature data were developed from stable isotope analyses of plant cellulose in packrat middens. Our paleotemperature curve for the past twenty thousand years matches trends in regional July temperatures simulated by the National Center for Atmospheric Research, Community Climate Model, but the model greatly underestimates the magnitude of temperature changes.

REPORTS PUBLISHED:

Betancourt, J. L., and Turner, R. M., 1988, Historic arroyocutting and subsequent channel changes at the Congress Street crossing, Santa Cruz River, Tucson, Arizona, in Whitehead, E. E., and others, eds., Arid lands today and tomorrow: Tucson, University of Arizona, Office of Arid Lands Studies, p. 1353-1371.

Turner, R. M., and Bowers, J. E., 1988, Long-term changes in populations of Carnegiea gigantea, exotic plant species and Cercidium floridum at the Desert Laboratory, Tumamoc Hill, Tucson, Arizona, in Whitehead, E. E., and others, eds., Arid lands today and tomorrow: Tucson, University of Arizona, Office of Arid Lands Studies, p. 445-455.

Van Devender, T. R., Thompson, R. S., and Betancourt, J. L., 1987, Vegetation history of the deserts of southwestern North America and adjacent areas during the last deglaciation: Boulder, Colo., Geological Society of America, The Geology of North America, v. K-3, p. 323-352.

Webb, R. H., Steiger, J. W., and Turner, R. M., 1987, Dynamics of Mojave Desert shrub assemblages in the Panamint Mountains, California: Ecology, v. 68, no. 3, p. 478-490.

WR164 ESTUARINE PLANKTON DYNAMICS

TITLE: Plankton Dynamics in Tidal Estuaries

PROJECT NUMBER: WR 79-164

LOCATION: San Francisco Bay area, CA

PROJECT CHIEF: Cloern, James E.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Because plankton are important sources of material and energy for other trophic levels, and because they interact rapidly with dissolved solutes, an understanding of plankton dynamics is a prerequisite for understanding other dynamic phenomena in estuaries. The composition and density of plankton populations vary temporally and spatially in response to natural and human-induced environmental changes. Therefore, assessments of human impact on estuarine ecosystems is dependent on a thorough understanding of the relation between natural environmental changes and plankton dynamics in unperturbed systems.

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 suggest important mechanisms that must be acknowledged by models and provide a data base for model calibration and subsequent verification. Conversely, evolving ecological models suggest processes and environmental factors that deserve particular emphasis by field studies. Feedback between model development and field work will accelerate understanding of the natural system, and should produce ecological models having sufficient realism to predict gross effects of human-induced perturbations.

PROGRESS: Articles were published on the following topics: (1) Seasonal and spatial patterns of primary production in Tomales Bay, Calif., (a pristine estuary north of San Francisco Bay, Calif.); (2) turbidity as a control of primary production in estuaries (an invited review paper); (3) a theoretical investigation of a mechanism of horizontal transport in bathymetrically complex basins; and (4) a ninth data report on hydrography/biology of South San Francisco Bay (covering years 1984-1986). Invited testimony was given at State of California hearings to set environmental standards for San Francisco

Bay. A multiagency study to characterize variability of salinity (a conservative tracer), phytoplankton biomass, and suspended sediment concentrations over short time and spatial scales in South San Francisco Bay was completed; two manuscripts are in review. Analysis of historic data suggests an event-scale mechanism for rapid horizontal mixing ("flushing") in South San Francisco Bay, that is driven by river pulses and tides; a manuscript is in preparation. A field investigation was completed during spring 1988 to characterize vertical mixing rates (microstructure measurements of water density) spatially and temporally in South San Francisco Bay. A program to measure biological production in northern San Francisco Bay as a response to the extreme drought of 1987-1988 was initiated. Significant advances were made in the development of a laboratory-flume technique to measure filter-feeding rates of intact benthic communities; the methodology should be available to begin a rigorous study of this important biological process in San Francisco Bay during the next year.

REPORTS PUBLISHED:

Smith, S. V., Wiebe, W. J., Hollibaugh, J. T., Dollar, S. J., Hager, S. W., Cole, B. E., Tribble, G. W., and Wheeler, P. A., 1987, Stoichiometry of C, N, P, and Si fluxes in a temperate-climate embayment: Journal of Marine Research, v. 45, p. 427-460.

Khorram, S., Catts, G. P., Cloern, J. E., and Knight, A. W., 1987, Modeling of chlorophyll a from an airborne scanner: IEEE Transactions on GeoScience and Remote Sensing, v. GE-25, p. 662-669.

Cloern, J. E., 1987, Review of the book, "Synthesis and Modeling of Intermittent Estuaries," by Cuff W. R., and Tomczak, Jr., M.: Marine Geology, v. 76, p. 332-333.

Zehr, J. P., Harvey, R. W., Oremland, R. S., Cloern, J. E., George, L., and Lane, J. L., 1987, Big Soda Lake (Nevada). 1. Pelagic bacterial heterotrophy and biomass: Limnology and Oceanography, v. 32, p. 781-793.

Cloern, J. E., Cole, B. E., and Wienke, S. M., 1987, Big Soda Lake (Nevada). 4. Vertical fluxes of particulate matter - seasonality and variations across the chemocline: Limnology and Oceanography, v. 32, p. 815-824.

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Powell, T. M., Willmot, S., Murray, J. D., Manoranjan, V. S., and Cloern, J. E., 1988, Transient spatial patterns in plankton communities: blooms and traveling waves of phytoplankton in estuaries, in Hallam, T. G., Gross, L. J., and Levin, S. A., eds., 1986 Proceedings of Triest Research Conference on Mathematical Ecology: World Scientific Publishing, p. 236-267.

Alpine, A. E., Wienke, S. M., Cloern, J. E., and Cole, B. E., 1988, Plankton studies in San Francisco Bay. IX. Chlorophyll distributions and hydrographic properties in South San Francisco Bay, 1984-1986: U.S. Geological Survey Open-File Report 88-319, 86 p.

WR174 MICROBIAL BIOGEOCHEMISTRY

TITLE: Microbial Biogeochemistry of Aquatic Environments

PROJECT NUMBER: WR 81-174

LOCATION: Topical Research

PROJECT CHIEF: Oremland, Ronald S.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Micro-organisms alter the chemistry and fertility of aquatic systems by performing complex transformations of organic and inorganic molecules. The biogeochemical mechanisms by which these transformations proceed and their quantitative significance to the cycling of elements in the biosphere is understood poorly. In addition, microbes are geochemically active in environments representing biological extremes, such as volcanoes, hotsprings, spreading centers, and hypersaline waters, and at both low and high values of pH.

OBJECTIVE: Develop conceptual models of biogeochemical transformations and measure their quantitative importance in aquatic environments. Measure rates of biologically mediated geochemical reactions in volcanic regions and in other environments representing biological extremes. Compare these measurements and pathways to similar reactions occurring in aquatic environments that do not represent biological extremes.

APPROACH: Study pathways of biogeochemical transformations mediated by micro-organisms in the laboratory using materials taken from the environment (for example, sediments). Conduct biochemical experiments with isolated cultures of micro-organisms responsible for these transformations and determine their overall significance to the cycling of elements in aquatic environments. Use these in situ measurements to discriminate between purely chemical reactions and biologically mediated reactions that occur in geothermal or volcanic regions and other extreme environments.

PROGRESS: Continued investigations on the biogeochemistry of Mono Lake, Calif., revealed the following new information: (1) A small phytoplankter is responsible for 50 percent of annual productivity. This organism has an unusual vertical distribution, and its behavior is borne out by its unique physiology. (2) Significant N_2 fixation occurs in the littoral zone of the lake, being carried out by algal/bacterial associations. (3) The vertical integrity of the recent meromixis is breaking down after 5 years as evidenced by chemical data. (4) Sulfate reduction and methanogenesis in the water and sediments mineralize about 50 percent of primary productivity. (5) Methane flux from these and other lakes were studied with regard to several physical factors. Selenate and selenite confer a bacteriostatic effect on bacteria, which can be ameliorated to some degree by sulfur compounds. Reduction of selenate by anoxic sediments proceeds by the formation of elemental selenium.

The microbes responsible for this process are probably nitrate or manganese reducing bacteria. This discovery is of great significance towards understanding the biogeochemistry of Se in impacted environments like Kesterson.

REPORTS PUBLISHED:

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Smith, R. L., and Oremland, R. S., 1987, Big Soda Lake, Nevada. 2. Pelagic sulfate reduction: Limnology Oceanography, v. 32, p. 794-803.

Iversen, N. I., and others, 1987, Big Soda Lake, Nevada. 3. Pelagic methanogenesis and anaerobic methane oxidation: Limnology Oceanography, v. 32, p. 804-814.

Oremland, R. S., and others, 1987, Sources and flux of natural gases from Mono Lake, California: Geochim. Cosmochim. Acta, v. 51, p. 2915-2929.

Fischer, C. R., and others, 1987, The importance of methane and thiosulfate in the methabolism of the bacterial symbionts of two deep sea mussels, Mas. Biol, v. 96, p. 59-72.

Oremland, R. S., and Capone, D. G., 1988, Use of "specific" inhibitors in biogeochemistry and microbial ecology: Advanced Microbial Ecology, v. 10, p. 285-383.

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Oremland, R. S., 1988, The biogeochemistry of methanogenic bacteria, in Zehnder, A. J. B., ed., Biology of anaerobic microorganisms: J. Wileg & Sons, p. 641-702.

Oremland, R. S., and others, in press, Microbial and biogeochemical processes in Big Soda Lake, Nevada, in Kelts, K., and Fleet, A., eds., Lacushine petroleum source rocks: London, Geol. Soc.

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WR186 BIOTA-SOLUTE TRANSPORT INTERFACE

TITLE: Biotic Interface with Fluvial Transport: Processes Associated with Dissolved Solutes in Transport

PROJECT NUMBER: WR 84-186

LOCATION: California Statewide

PROJECT CHIEF: Triska, Frank J.

HEADQUARTERS OFFICE: Menlo Park, CA

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 biotic transformations and adsorption of transported solutes are prerequisites for understanding both the biological structure and nutrient chemistry of streams and rivers. Specific chemical transformations and their rates, biotic community structure, and background water chemistry vary spatially and temporally along the drainage network. Comparison of biotic response to solutes in transport between pristine and anthropogenically modified riverine environments is understood poorly, but the comparison is necessary for long-term management of these 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, and floodplains.

APPROACH: Use laboratory experiments on communities collected from small to large streams and use in situ field experiments to estimate biotic transformation of dissolved solutes. Conduct field experiments both at background concentrations, and with mixtures of conservative and nonconservative solutes injected into pristine and human-impacted fluvial environments. Examine environmental factors regulating process rates (solute concentration, temperature, light, current velocity, and biotic interactions) in relation to biotic transformation of transported solutes. Emphasize cycling of elements which have high assimilative demand and can subsequently be passed to higher trophic levels (that is, carbon, nitrogen, phosphorous). Project orientation emphasizes process rates rather than community structure. Cooperate with other projects interested in biogeochemical cycling and biotic-abiotic transport interactions.

PROGRESS: A simulation model of algal nitrate uptake developed from studies using flow-through microcosms has been extended to field data of nitrate uptake/transport from a pristine third order stream, Little Lost Man Creek, Humboldt Co., Calif. Early results of this work by A. Jackman (University of California, Davis) predicted significantly higher nitrate

concentration in ground water than channel water to support biotic production. Model predictions are consistent with subsequent observations from bankside subsurface flows, and with studies of bacterial nitrification potential. The field experiments indicate high potential nitrate production in saturated aerobic habitats approximately 2-4 m laterally from the wetted channel under base flow conditions. In a sewage-contaminated sand and gravel aquifer (Otis Air Force Base, Mass.), it was found that close interval sampling is necessary to delineate chemical and microbiological gradients in ground-water studies. In situ denitrification can serve as an important mechanism for nitrate removal from contaminated ground water. Dominance of denitrification as the terminal electron acceptor is reflected in the geochemistry of dissolved gases. In a permanently ice-covered lake (Lake Fryxell, Antarctica) productivity was estimated and dissolved gases and chemical profiles determined. Initial results suggest rapid growth of a blue-green algal population over short time periods. Dissolved organic carbon (DOC) profiles suggest that degradation of algal derived organic material in lake sediments is an important DOC source in these lakes.

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Smith, R. L. and Duff, J. H., in press, Denitrification in a sand and gravel aquifer: Journal of Applied and Environmental Microbiology, v. 54.

WR190 SOLUTE TRANSPORT INVOLVING BIOTA

TITLE: Solute Transport Involving Biological Processes in Surface Waters

PROJECT NUMBER: WR 86-190

LOCATION: Topical Research

CHIEF: Kuwabara, James S.

CITY: Menlo Park, CA

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/dissolution, sorption and redox. Each of these processes affect and are 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 inorganic solutes between particulates and primary producers. Examine and quantify processes controlling that transport (for example, adsorption onto and desorption from particulates and uptake and release from plankton and periphyton). Conduct laboratory studies using chemically defined particles and formulate a conceptual representation of the processes. Conduct culture experiments using chemically analyzed natural sediment samples to verify and calibrate these models. 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 particulates and dissolved phases and to identify potentially important biological transport processes. Determine trace metal, macronutrient and organic carbon concentrations using various preparative techniques. Use chemically defined particles and unialgal cultures to describe processes controlling solute uptake and release by cells. Conduct laboratory culture experiments using field samples of suspended particulates and isolates from natural planktonic and periphyton populations and generate biological transport submodels for testing and eventual incorporation into comprehensive water-quality models.

PROGRESS: Reports have been submitted for journal publication or are in preparation presenting trace metal studies in South San Francisco Bay. A collaborative study between four research projects in the Water Resources Division and one project in the Geologic Division investigated processes affecting trace metal distribution during and after the annual spring phytoplankton bloom of 1985. Results suggest that (1) chemical speciation of copper and zinc was controlled by complexation with dissolved organic matter, (2) suspended particles may serve as a source of dissolved cadmium, and (3) elevated metal free ion concentrations in the water column may affect phytoplankton community structure in the South Bay in favor of metal tolerant species. Initial work within the Lake Tahoe Basin has been extended to include collaboration with Lake studies at the University of California at Davis. This work is investigating controls on the biovailability of particle-bound solutes in this chemically-diverse environment, which has experienced exponential increases in primary production during the last two decades. Three timescales of variability in chemical data have been observed (1) diurnal fluctuations due to air temperature and stream discharge variability (and possibly photochemistry); (2) fluctuations occurring over a timescale of days (i.e., over the snow melt period); and (3) seasonal fluctuations that contrast high and low flow conditions. These fluctuations will be more closely characterized in the context of trends in lake primary productivity. An allpolypropylene (i.e., autoclavable) hollow fiber dewatering device has been developed for use at this and other project sites. Initial testing of this device by microbial enumeration and processing and analyses of standard particles of known chemical composition indicate that this device provides a very useful alternative to other dewatering systems for trace inorganic analyses of suspended particles. Continuing arsenic (As) studies at Whitewood Creek, S. Dak., have focused on the role of periphyton on As transport along the Creek. A few new observations are noteworthy (1) the succession of periphyton species from one year to the next can be drastically different (we have thus far only sampled during two summers); (2) accumulation of As by various dominant species is significantly different (that is, biologically related solute transport parameters have various scales of temporal variability); and (3) algal uptake of both orthophosphate and arsenate are appropriately modeled by first order rate equations.

REPORTS PUBLISHED:

Kuwabara, J. S., and Helliker, P., 1988, Trace contaminants in streams, in Cheremisinoff, P., ed., Encyclopedia of civil engineering practice: Technomic Press, v. 5, ch. 26, p. 739-766.

Kuwabara, J. S., and Robinson, J. R., 1988, Development of a hollow fiber tangential flow filtration system for concentration of suspended sediment samples from natural waters, in Mallard, G. E., ed., U.S. Geological Survey Toxic Substances Hydrology Program - Surface-Water Contamination, Proceedings of the Technical Meeting, Denver, Colorado, 1987: U.S. Geological Survey Open-File Report 87-764.

Kuwabara, J. S., Chang, C. C. Y., and Pasilis, S. P., 1988, Effects of algal growth on arsenic transport in Whitewood Creek, South Dakota, in Mallard, G. E., ed., Preliminary Results, U.S. Geological Survey Toxic Substances Hydrology Program - Surface-Water Contamination, Proceedings of the Technical Meeting, Denver, Colorado, 1987: U.S. Geological Survey Open-File Report 87-764.

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WR191 BACTERIA-CONTAMINANT INTERACTIONS

TITLE: Interaction of Bacteria with Environmental Contaminants and Solid Surfaces in the Aquatic Environment

PROJECT NUMBER: WR 86-191

LOCATION: Topical Research

PROJECT CHIEF: Harvey, Ronald W.

HEADQUARTERS OFFICE: Menlo Park, CA

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. Due to the persistence of some contaminants in the subsurface environment and to increasing demand 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. Since 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 more 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 upon subsurface transport of bacteria since the role of bacterial transport upon the fate of environmental contaminants in ground water is unknown.

APPROACH: The complex nature of interactions between bacteria and organic and inorganic contaminants in particle-laden aquatic habitats necessitates an approach involving both field and laboratory studies. (1) Study the influence of surfaces and interfaces upon microbial heterotrophic activity in particle-laden aquatic environments, including freshwater aquifers. (2) Study of the effect of organic contaminants upon the distribution, transport, and activity of the bacterial population in ground-water habitats. These studies will be performed jointly with Richard Smith, Water Resources Division, Denver. (3) Use flow-through column experiments, both to assess the role of adherent bacteria upon the mobility of selected heavy metals and toxic organic

compounds in simulated aquifer environments and to investigate factors affecting movement of bacteria through porous media. (4) Make microcosm studies of bacteria-heavy metal interactions.

PROGRESS: Small-scale natural and forced gradient ground-water tracer-injection experiments have continued at the Cape Cod Groundwater Contamination Study Site at Otis Air Force Base in Massachusetts. A protocol for investigating the distribution and significance of microbial eukaryotes in contaminated ground water was developed. Core samples of aquifer sediments taken along a transect through contaminated ground water have been assayed for bacterial heterotrophic activity "signature" lipids, respiratory pigments and bacterial biomass. Determinations of abundance and size distributions of indigenous bacteria as they are transported through the aquifer has enabled the testing of various hypotheses concerning the applicability of a colloid filtration model to problems of transport of indigenous bacteria. Preliminary data were collected on abundance, distribution, and diversity of the Protozoan community in the contaminant plume. Progress has continued on a series of interpretative reports on bacterial growth, transport activity, and predation in an organically-contaminated aquifer.

REPORTS PUBLISHED:

Harvey, R. W., 1987, A fluorochrome-staining technique for counting bacteria in saline, organically enriched, alkaline lakes: Limnology and Oceanography, v. 32, p. 993-995.

Zehr, J. P., Harvey, R. W., Oremland, R. S., Cloern, J. C., George, L., and Lane, J. L., 1987, Big Soda Lake (Nevada). I. Pelagic bacterial heterotrophy and biomass: Limnology and Oceanography, v. 32, p. 781-793.

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Smith, R. L., Harvey, R. W., Duff, J. H., and LeBlanc, D. R., 1987, Importance of close-interval vertical sampling in delineating chemical and microbiological gradients in ground-water studies: U.S. Geological Survey Open-File Report 87-109.

WR192 ESTUARINE BENTHIC COMM. DYNAMICS

TITLE: Environmental Influences on Estuarine Benthic Community Dynamics

PROJECT NUMBER: WR 86-192

LOCATION: Topical Research

PROJECT CHIEF: Nichols, Frederic H.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: 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/abundance changes. Thus, they are often used as water-quality indicators. However, their use in water-quality studies requires that communities remain at steady state, except when influenced by human activity. Long-term studies show that natural variation over a variety of timescales often mask human-induced changes. Also, 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: Characterize long-term patterns in estuarine and coastal benthic communities. 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. Assess the contribution of human activity (waste contamination, control of river runoff) to the remaining unexplained variability in community dynamics. Measure, through field and laboratory studies, the processes which determine the rates at which invertebrates remove phytoplankton from the water column.

APPROACH: 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. 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 using transplanted animals, and through laboratory experiments using individual species and intact infaunal communities in flumes that simulate changing field conditions.

PROGRESS: A report that was completed on long-term changes in a deep Puget Sound benthic community demonstrates that some of the changes that occurred over the 24-year period of study at one site were mirrored at two other locations. The results suggest that the changes at the initial site near a waste outfall were not necessarily localized events that might be associated with the waste inputs. A report was completed on the probable link between behavior of a dominant infaunal invertebrate on the California continental shelf and alongshore current reversals during the upwelling season which results in a temporarily enhanced food resource. After a long period of system development in order to achieve healthy growth of algae in the recirculating seawater flume system, a near-total reconstruction of the flume was completed and initial experiments were conducted to demonstrate the utility of such a system in measuring the removal of phytoplankton by benthic invertebrates in a physically realistic manner. Experiments are being conducted to measure grazing rates of "seeded" populations under different flow regimes in preparation for studies "seeded" populations of undisturbed field populations. A study was begun on the possible consequences of drought and increased metal availability to reproduction in the clam Macoma balthica, with the goal of developing a stress marker. Studies were begun of Potamocorbula sp., a clam newly introduced to San Francisco Bay from Asia that is spreading rapidly and widely throughout northern San Francisco Bay, and that may have major ecological consequences for the estuary's food web. These studies include quantitative studies of its distribution, mode/timing of reproduction, and secondary production.

REPORTS PUBLISHED:

Nichols, F. H., in press, Long-term changes in a deep Puget Sound benthic community: local or basin-wide?: Proceedings, First Annual Puget Sound Research Conference.

Hopkins, D. R., 1987, Temporal variations in the benthic communities at four intertidal sites in San Francisco Bay, Calif., 1983-1985: U.S. Geological Survey Open-File Report 87-387, 89 p.

Nichols, F. H., 1987, Benthic ecology and heavy metal accumulation, in Goodrich, D. M., ed., San Francisco Bay: issues, resources, status, and management: National Oceanic Atmospheric Administration Estuary-of-the-month Seminar Series No. 6, Proceedings of a seminar held November 22, 1985, Washington, D.C., p. 65-68.

Thompson, J. K., and Nichols, F. H., 1988, Food availability controls the seasonal cycle of growth in the bivalve Macoma balthica: Journal of Experimental Marine Biology and Ecology, v. 116, p. 43-61.

GEOMORPHOLOGY AND SEDIMENT TRANSPORT

CR098 SEDIMENT TRANSPORT PHENOMENA

TITLE: Measurement and Prediction of Sediment Transport Phenomena

PROJECT NUMBER: CR 74-098

LOCATION: Topical Research

PROJECT CHIEF: Stevens, Herbert H., Jr.

HEADQUARTERS OFFICE: Lakewood, CO

PROBLEM: In alluvial streams, for every different hydrologic condition, the bed configuration, sediment transport, and hydraulic characteristics mutually change to achieve quasi-equilibrium. These changes affect the ability of the stream to convey given quantities of water, accommodate navigation, transport and dilute solid and solute wastes, support aquatic biota, and perform a variety of other similar functions. As yet, the relation between pertinent hydraulic and sedimentologic variables are not completely understood. Hence, the extent to which important variables, particularly bedform roughness and sediment transport, will change in response to natural or man-induced alterations to the flow regime cannot be predicted with desired reliability. As a result, optimum utilization and management of a waterway usually is not assured. Often, modifications intended to enhance the utility of a waterway are ineffective or have adverse effects. Lack of understanding is due in part to inadequate instrumentation for measuring the bedload transport. This problem is particularly acute in areas where resources are being mined for energy development.

OBJECTIVE: Provide a more complete understanding of sedimentation phenomena in alluvial streams and the response of such streams to imposed changes through the use of improved instrumentation. In particular, consider the interrelationships between bed-form characteristics and the transport of bedload and bed-material load.

APPROACH: Initially, analyze existing data to relate bed-form characteristics to the conditions of flow and sediment transport, and develop one or more bedload samplers to permit accurate measurements of bedload transport. The development of bedload samplers will be accomplished through a comprehensive testing and calibration program with prototype samplers in a specifically designed laboratory facility capable of continuously measuring the discharge of bedload particles from 2 to 64 millimeters in diameter under different flow conditions. Later, study the characteristics of bed-forms, sediment transport, and other pertinent variables as required to meet specific needs. Use acoustic instrumentation, including side-scan sonar, to measure bed-form configuration and movement. Use suitable bedload samplers, and suspended load samplers, to define transport rates. Finally, analyze information to define criteria for predicting bed-form morphology and to provide a better understanding of sediment-transport phenomena in both sand-bed and gravel-bed streams.

PROGRESS: Data collected during laboratory calibration of bedload samplers were used to develop a procedure to reduce the number of bedload samples required to define the mean bedload discharge. Additional refinement on the procedure is required. Two sets of computer programs for compiling measurements data and computing fluvial sediment discharge by five existing bedload discharge formulas and nine existing bed-material formulas have been developed and are available; one set of programs is for use with a minicomputer and the other set is for use on microcomputers.

REPORTS PUBLISHED:

Hubbell, D. W., and Stevens, H. H., Jr., 1987, Cascade-sieve shaker for rapid particle-size analysis of coarse sediment, in Selected Papers in Hydrologic Sciences: U.S. Geological Survey Water-Supply Paper 2310, p. 73-85.

Hubbell, D. W., Stevens, H. H., Jr., Skinner, J. V., and Beverage, J. P., 1987, Closure for new approach to calibrating bedload samplers: American Society Civil Engineers, Hydraulics Division Journal, v. 113, no. 7, p. 941-942.

CR102 SEDIMENT IN RIVERS

TITLE: Movement and Storage of Sediment in River Systems

PROJECT NUMBER: CR 75-102

LOCATION: Nationwide

PROJECT CHIEF: Meade, Robert H.

HEADQUARTERS OFFICE: Lakewood, CO

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 a thousand. 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 in the upper Missouri River basin; and (3) assess sources, pathways, and sinks by intensive field studies (including tracer studies) of selected small rivers.

PROGRESS: A new project on sediment and pollutants in Mississippi River was organized and two sampling cruises between St. Louis and New Orleans were completed. A resurvey of cross sections in Powder River, Mont., showed small to moderate amount of channel change since last year. Analysis of arsenic concentration and grain size of 200 samples collected in the floodplain of Belle Fourche River, S. Dak., showed aerial and stratigraphic distributions of contaminated sediments.

WRD FEDERAL RESEARCH PROJECTS.....GEOMORPHOLOGY & SEDIMENT TRANSPORT

REPORTS PUBLISHED:

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Meade, R. H., in press, Movement and storage of sediment in river systems, in Lerman, A., and Meybeck, M., eds., Physical and chemical weathering in geochemical cycles: Dordrecht, Netherlands, Reidel Publishing Company.

Meade, R. H., Yuzyk, T. R., and Day, T. J., in press, Movement and storage of sediment in rivers of the United States and Canada, in Wolman, M. C., and Riggs, H. C., eds., Surface water hydrology: Geological Society of America, The Geology of North America, v. O-1.

Nolan, K. M., and Marron, D. C., in press, Response of the Redwood Creek stream channel to storms and landuse, 1936-82, in Nolan, K. M., Kelsey, H. M., and Marron, D. C., eds., Geomorphic processes and aquatic habitat in the Redwood Creek basin, northwestern California: U.S. Geological Survey Professional Paper 1454.

Nolan, K. M., Kelsey, H. M., and Marron, D. C., in press, Summary of research in the Redwood Creek Basin, in Nolan, K. M., Kelsey, H. M., and Marron, D. C., eds., Geomorphic processes and aquatic habitat in the Redwood Creek basin, northwestern California: U.S. Geological Survey Professional Paper 1454.

Nolan, K. M., and Marron, D. C., in press, Stream channel response to the January, 1982, storm in the Santa Cruz Mountains, in Wieczorek, G. F., and Ellen, S. D., eds., Landslides, flooding and marine effects of the storm of January 3-5, 1982, in the San Francisco Bay area: U.S. Geological Survey Professional Paper 1434.

Marron, D. C., and Landon, J. A., 1987, Susceptibility to mudflows in the vicinity of Lassen Peak, California, in Subitzky, S., ed., Selected papers in the hydrologic sciences 1986: U.S. Geological Survey Water-Supply Paper 2310, p. 97-106.

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Marron, D. C., 1988, Effects of sediment transport and depositional processes on the distribution and longevity of a metal-contaminating problem in west-central South Dakota: The Earth Scientist, v. 5, no. 2, p. 3-8.

CR105 CHANNEL MORPHOLOGY

TITLE: Effects of Water and Sediment Discharges on Channel Morphology

PROJECT NUMBER: CR 65-105

LOCATION: Topical Research

PROJECT CHIEF: Williams, Garnett P.

HEADQUARTERS OFFICE: Lakewood CO

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

OBJECTIVE: Determine and analyze the influence of the major variables, particularly water and sediment discharges, governing channel morphology.

APPROACH: Study the effect of large contributions of sediment to stream channels. Make field surveys and aerial-photograph analysis, preferably time-sequential, of stream reaches that have received exceptionally large sediment inputs. Document channel response, with a view towards eventually developing a general model of channel response.

PROGRESS: Bivariate relations between annual sediment yield (tons/year drainage area) and drainage-basin area are spurious because drainage-basin area is common to both variables. Two alternative methods for portraying the annual suspended-sediment load of a river were examined. One method consists of plotting suspended-sediment load (tons/year) against distance downstream. Such plots indicate that annual suspended-sediment load does not necessarily have a linear relationship with distance. The second method consists of plotting annual suspended-sediment load against drainage-basin area. Both methods more accurately portray fundamental relations between annual sediment load and drainage-basin characteristics than does the yield-area relation because spurious correlation is avoided. The suspended-sediment loads of many rivers have been found to be in phase downstreamward from year to year when considered for time scales of 10 to 15 years.

WRD FEDERAL RESEARCH PROJECTS.....GEOMORPHOLOGY & SEDIMENT TRANSPORT

REPORTS PUBLISHED:

Troutman, B. M., and Williams, G. P., 1987, Fitting straight lines in the earth sciences, in Size, W. B., ed., Use and abuse of statistical methods in the earth sciences: New York and Oxford, Oxford University Press (International Association for Mathematical Geology Studies in Mathematical Geology No. 1), p. 107-128.

Williams, G. P., and Troutman, B. M., 1987, Algebraic manipulation of equations of best-fit straight lines, in Size, W. B., ed., Use and abuse of statistical methods in the earth sciences: New York and Oxford, Oxford University Press (International Association for Mathematical Geology Studies in Mathematical Geology No. 1), p. 129-141.

Williams, G. P., 1988, Paleofluvial estimates from dimensions of former channels and meanders, in Baker, V. R., Kochel, R. C., and Patton, P. C., eds., Flood Geomorphology: New York, Wiley, p. 321-334.

Williams, G. P., and Costa, J. E., 1988, Geomorphic measurements after a flood, in Baker, V. R., Kochel, R. C., and Patton, P. C., eds., Flood Geomorphology: New York, Wiley, p. 65-77.

CR187 BEDLOAD TRANSPORT RESEARCH

TITLE: Hydraulics and Mechanics of Bedload-Transport Processes

PROJECT NUMBER: CR 74-187

LOCATION: Topical Research

PROJECT CHIEF: Emmett, William W.

HEADQUARTERS OFFICE: Lakewood, CO

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 knowledge is available regarding the hydraulics and mechanics of bedload transport. Before continuing advances in river channel behavior can be made, additional understanding of the behavior of bedload sediment must be made.

OBJECTIVE: (1) Define spatial and temporal variations in bedload-transport rate for a single stage of flow; (2) define change in average magnitude of transport rate over a range in flow; (3) define change in average magnitude of transport rate over a range in channel geometry; and (4) analyze the data to evaluate the applicability of available bedload equations, suggest new coefficients for the existing equations, or propose new relations for predicting rates of bedload transport.

APPROACH: Use the conveyor-belt bedload-transport facility on the East Fork River near Pinedale, Wyo., as a control to evaluate variability factors in bedload transport and to field calibrate the Helley-Smith bedload sampler; use the calibrated Helley-Smith sampler in the systematic collection of bedload samples, making concurrent measurements of streamflow characteristics from a variety of sand- and gravel-bed streams; and, within the laws of general physics, develop empirical relations of bedload transport and interpret the physical significance of these relations. Initiate a tracer study utilizing fluorescent particles at the conveyor-belt bedload-trap research facility to evaluate (1) residence time of sediment, (2) average speed of particles, (3) depth of bed material involved in transport, (4) dispersion of bed material, (5) short-term channel changes accompanying sediment transport, (6) influence of availability of sediment on transport rate, and other related aspects of sediment transport.

PROGRESS: Measurements of bedload transport and associated hydraulic characteristics have been completed for the East Fork River, Wyo. Equipment and procedures have been described and data are being analyzed and interpreted. In addition, six field sites have been selected and bedload data are being collected at these sites by operational units of the Water Resources Division. In addition to these six sites and the East Fork River site, data from several other sites are providing information to the core data base.

WRD FEDERAL RESEARCH PROJECTS.....GEOMORPHOLOGY & SEDIMENT TRANSPORT

REPORTS PUBLISHED:

Emmett, W. W., and Averett, R. C., in press, Fremont Lake, Wyoming--Some aspects of the inflow of water and sediment: U.S. Geological Survey Water-Resources Investigations Report 88-4021.

CR266 ESTUARY SEDIMENTATION/EUTROPHICATION

TITLE: Transport and Deposition of Sediments and Sediment-Borne Contaminants in Tidal Rivers and Estuaries

PROJECT NUMBER: CR 81-266

LOCATION: Topical Research

PROJECT CHIEF: Glenn, Jerry L.

HEADQUARTERS OFFICE: Lakewood, CO

PROBLEM: Sediments that contain large concentrations of nutrients and trace metals are accumulating rapidly in part of the tidal Potomac River, the Potomac Estuary, and the adjacent marginal embayments. Accumulations of sediments and sediment-borne contaminants may limit significantly the use of tidal waters and estuaries for commercial, recreational, and aquacultural purposes. The sediments decrease channel depths and widths to the detriment of commercial and recreational interests, and cover and destroy productive shellfish grounds. The nutrients are a factor in the development and maintenance of undesirable eutrophic conditions, including nuisance algae blooms and low levels of dissolved oxygen. Sedimentation and eutrophication problems in the Potomac are a consequence of essentially uncontrollable natural and anthropogenic influences. The problems began to develop naturally several thousand years ago when the current rise in sea level drowned the Potomac River and began the evolution of the modern tidal river-estuary system.

OBJECTIVE: (1) Identify modern sources of sediments and nutrients; (2) establish changes with time in sources or supply rates due to natural and anthropogenic influences; (3) determine sediment and nutrient transport and deposition patterns; (4) compute rates of accumulation and amounts of sediments and nutrients in selected hydrologic and geomorphic divisions of the Potomac system; and (5) compare supply and accumulation rates for prehistorical and historical periods with contemporary rates from concurrent transport studies.

APPROACH: Determine areal and stratigraphic distributions of sediments, nutrients, and trace metals by a combination of direct sampling (surface and core) and remote sensing (side-scan sonar and subbottom profiling). Analyze sediment samples for indicators of sources (particle size, mineralogy, nutrient and trace-metal concentrations) and accumulation rates (lead-210, carbon-14 pollen concentrations and distributions). Estimate sediment contributions from the shoreline source using a combination of field mapping, monitoring, and sampling at selected sites, and using laboratory measurements from available air photographs and maps. Integrate data with results from measurements and models of modern sediment and nutrient transport to provide past and present sediment and nutrient budgets for selected Potomac reaches.

PROGRESS: Although phosphorus concentrations in bottom sediments collected in the transition area of the tidal Potomac system, and exposed to the water column from the estuary showed extreme variability after a short period of exposure, the variability was traced to laboratory procedures rather than to phosphorus uptake or release. In fact, preliminary analyses of new data indicate that phosphorus is released only slowly when sediments are transported from an oxic transition environment to an anoxic estuary environment. Channel margin sediments along the Mississippi River are mainly sands with a variety of surface bedforms ranging from dunes to ripples; fine sediments are found in sheltered areas or in thin deposits that accumulate on banks and bars during falling stages. Overbank deposits between the channel and the mainline levees range from fine sands on natural levees to silts and clays in abandoned channels and backswamps.

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CR273 HYDROLOGICAL-BIOLOGICAL INTERACTIONS

TITLE: The Interface of Hydrological and Biological Processes in Rivers

PROJECT NUMBER: CR 82-273

LOCATION: Topical Research

PROJECT CHIEF: Andrews, Edmund D.

HEADQUARTERS OFFICE: Lakewood, CO

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. 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, river-channel adjustments in response to land-use activities such as surface mines, reservoirs, and urbanization, can be longer than the duration of the watershed change. In watersheds where various land use changes occur every several years, the river channel may be continually adjusting to a different supply of water and sediment, and thus, never reach a quasi-equilibrium condition. In these rivers, the period of instability is the only significant condition. Consequently, an understanding of the dynamics and rate of river channel adjustment from one quasi-equilibrium state to another is very important to managing fluvial resources. A wide range of social and economic costs may result from substantial river channel changes. One of the most frequent and important adverse impacts is damage to the aquatic ecosystem. Aquatic organisms depend on a particular combination of hydraulic characteristics (that is, their physical habitat) to meet life requirements. When a river channel adjusts to a change in its watershed, the physical habitat of the aquatic organisms in the river may be reduced or even eliminated, either during the period of instability or in the future quasi-equilibrium condition. To evaluate the biological effects of watershed alternation, hydrologists frequently need to predict the hydraulic geometry and channel pattern at various times in the future so that changes in the physical habitat can be assessed. In many ways, such an analysis of physical habitat concerns the same questions

one would address in an evaluation of the effects of channel change on engineering works, or navigation. On the other hand, certain aspects of river channel changes are of greater importance to the aquatic ecosystem than the integrity of engineering works. The primary focus of this research project is to understand the dynamics and rate of river channel change as they affect the physical habitat. The results, however, will no doubt contribute to understanding the broader question of river channel adjustment. The greatest deficiencies in our present knowledge of river channel adjustment as it relates to the aquatic ecosystem are (1) the longitudinal sorting of bed material, especially gravel, (2) the formation of gravel bars, (3) adjustment of channel width, and (4) the rates at which the several hydraulic variables adjust.

OBJECTIVE: Describe the physical processes and rate at which a river channel adjusts due to a change in the water discharge, sediment size and sediment load supplied to the channel. Concentrate, in particular, on 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 that control these characteristics of river channels as well as the rate at which they function. Then, based upon an appreciation of these processes, formulate mathematical models of the processes as required for longitudinal routing of water and sediment. Ultimately, develop new analytical tools for describing river channel adjustment.

APPROACH: The ideal approach for this investigation would be to observe 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. However, this is impractical because adjustment of a river chanel may extend from a few decades to a century. Instead, two basic types of field studies will be combined. First, the movement of bed material through a reach of channel will be studied in detail. These investigations will consider the transport of bed material, distance transported, and location (bed, banks, or bar) of deposition for each size fraction. By use of measured bedload and suspended-transport rates, detailed measurements of flow structure, and mapping of channel features, the movement of bed material through the study reaches will be described. To the extent possible, these observations will be generalized to formulate a physically correct model of sediment movement by size fraction. The second part of this investigation will involve reconstructing the sequence and rate of adjustment for historical examples of river channel change. Because of the lack of detailed hydraulic measurments, this portion of the investigation may, at times, be somewhat descriptive and qualitative. These observations, however, will be vitally important as they will provide the temporal context in which to view the hydraulic characteristic at a particular point in time.

PROGRESS: An understanding of the interactions between flow over a spatially nonuniform sediment bed and the deformation of that bed is of fundamental importance to the study of rivers and estuaries. To study the salient physical processes which form the topography of erodible beds, the problem has been divided into two categories: bedforms, for which the bed instability and equilibrium morphology is primarily related to changes in vertical structure of the flow field, and bars; for which horizontal variations in the structure of the flow field are of primary importance. In each of these two cases, physically-based, predictive models for velocity and boundary shear stress fields have been developed. In the case of channel bars, the model accurately predicts flow structure through reaches with nonuniform curvature and complex bed topography. The bedform flow model treats changes in vertical flow structure associated with flow separation from a regular sequence of obstructions having gentle stoss and steep lee faces. These models have been verified using carefully collected data. The bar problem was addressed by using measurements made by other investigators; the bedform problem required the design and execution of a laboratory experiment. This bedform experiment yielded one of the most comprehensive and detailed set of velocity data over two-dimensional dune currently available. Subsequently, these models have been used to examine processes responsible for the evolution of the most common large-scale topographic features in rivers. The horizontal flow adjustment model has been used to understand the formation and stability of point bars in initially flat, curved channels, as well as the growth and equilibrium morphology of alternate bars in initially flat, straight channels. The vertical flow adjustment model has been employed to predict various aspects of the flow-bed coupling responsible for the initiation of bedforms, as well as the finite amplitude effects responsible for the height and wavelength of fully developed dunes.

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CR309 MISSISSIPPI RIVER SEDIMENT POLLUTANTS

TITLE: Sediment-Transported Pollutants in the Mississippi River

PROJECT NUMBER: CR 87-309

LOCATION: Topical Research

PROJECT CHIEF: Meade, Robert H.

HEADQUARTERS OFFICE: Lakewood, CO

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

APPROACH: Three to four boat trips per year, beginning above St. Louis and ending at New Orleans, 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 constitutents, both natural and manmade.

PROGRESS: Two sampling trips on the Mississippi between St. Louis and New Orleans were made in July-August and November-December 1987. Comprehensive new procedures were developed and tested for separating suspended sediment from large volumes of river water and for further subdividing the suspended sediment into three to four size fractions for individual chemical analyses. Initial results suggest that 0.5 percent of the United States annual production of atrazine is transported down the Mississippi River.

CR311 SEDIMENT IMPACTS FROM DISTURBED LANDS

TITLE: Geomorphic and botantical impacts of sediment due to natural and unnatural land disturbance

PROJECT NUMBER: CR 79-311

LOCATION: Topical Research

PROJECT CHIEF: Osterkamp, Waite R.

HEADQUARTERS OFFICE: Lakewood, CO

PROBLEM: Increased sediment yields from naturally stressed areas, such as mass-movement sites and devegetated lands, and man-stressed areas, such as mine spoils, urban areas, and agricultural lands, is one of the largest problems being addressed by agencies such as the U.S. Office of Surface Mining and U.S. Soil Conservation Service. The acquisition and interpretation of sediment data are among the most deficient areas that must be considered by these agencies. The impacts on geomorphology and botany that are caused by natural and induced sediment movement are sometimes intense; knowledge of these impacts is beneficial for understanding the effects of naturally occurring sediment movement.

OBJECTIVE: (1) Predict movement of sediment from naturally and unnaturally disturbed areas; (2) assess existing techniques and develop new ones based on geomorphic, botanical, and statistical principles as aids in improving interpretive capabilities; and (3) evaluate geomorphic, botanic, and hydrologic changes changes caused by sediment movement from disturbed areas.

APPROACH: (1) Develop techniques for determining the amounts and rates of sediment movement from disturbed areas based on factors such as land use, runoff, basin and landform morphology, and botanical indicators; (2) conduct research on the effects on landforms and vegetation of sediment movement using vegetation age, damage, and patterns of occurrence as indicators of the magnitude, frequency, and time of occurrence of destructive hydrologic events; (3) investigate the influence that ground-water movement exerts on sediment transport and changes in landforms by analyzing near-surface and subsurface rates of water and sediment movement (including piping, sapping, and seepage erosion) in dynamic hydrologic systems; and (4) conduct research on the interactions between hydrology, water chemistry, and geochemistry as determinants of sediment movement through a hydrologic system, in conjunction and close coordination with other research and District personnel.

PROGRESS: Studies of the magnitude and occurrence of debris flows on Cascade Range volcanoes are continuing. Field activities on Mount Shasta are largely completed; they have identified the frequency of occurrence of debris-flow deposits and have documented a variety of techniques useful for determining

the ages of the deposits. Final studies being made of Mount Shasta flows are considering the role that climatic factors have on the frequency of debris flows. Attention is now being shifted to Mount St. Helens and Mount Hood where similar studies will consider the role of ground-water movement to the initiation of debris flows. Channel-morphology studies are continuing in the Kansas River basin of Kansas and Nebraska, and in the Plum Creek basin of central Colorado. The Plum Creek work has demonstrated that channel narrowing results from processes of channel-island growth, in which expanding island sizes result in islands joining with each other and ultimately with the flood plain. These processes may be typical of the manner by which flood-widened sand channels of semiarid regions narrow through time. Continuing hydrologic studies of playa-lake basins on the Southern High Plains have suggested that the ephemeral lakes are active geomorphic features. A natural tracer, beryllium-ten, is present in high concentrations at depth at some sites, indicating that playa lakes may have been part of the Southern High Plains landscape since middle-Miocene time.

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CR313 SED.-WATER CHEM. IN LARGE RIVERS

TITLE: Sediment-Water Chemistry in Large River Systems: Biogeochemical, Geomorphic, and Human Controls

PROJECT NUMBER: CR 88-313

LOCATION: Topical Research

PROJECT CHIEF: Stallard, Robert F.

HEADQUARTERS OFFICE: Lakewood, CO

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 both erosion and the subsequent transport of material by rivers are mediated by a wide variety of highly-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. The problem is to develop a comprehensive and integrated description, through field and theoretical studies, 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 the 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 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. As part of these investigations, undertake field surveys, design sampling and analytical procedures, and create computer tools to manipulate and model data. Formulate smaller-scale field and laboratory studies to aid data interpretation where deemed necessary.

WRD FEDERAL RESEARCH PROJECTS.....GEOMORPHOLOGY AND SEDIMENT TRANSPORT

PROGRESS: Project began in FY 1988 and research is evolving from work begun at Princeton University. Sediment-water chemical interactions in the Mississippi and Orinoco river systems are being studied with emphasis on describing how the compositions of dissolved and solid loads in the mainstem and tributaries relate to the geology and geomorphology of their respective catchments. Three field trips were made on the Mississippi where the sampling program is just beginning, and one on the Orinoco, where sampling is ending. A laboratory is being established for sediment geochemistry; it will have facilities to prepare, under clean conditions, a wide variety of sediment samples for analysis by chemical dissection, x-ray diffraction, x-ray fluorescence, and particle imaging. In addition, a computer package for the interpretation of major and minor element data in rivers and ground waters is being designed; it will aid in the study of the role of weathering regime in sediment-water interaction in river catchments. Two related studies concerning weathering, erosion, and transport processes continue. One study investigates the biogeochemistry of tropical soils and examines how soil gas generation (with an emphasis on methane) is related to soil geochemistry and hydrologic regime; one field trip to Panama was undertaken during FY 1988. The other study involves collaborative work to develop an estuarine circulation model which will be used to examine the transport of sediment, nutrients, and trace metals in the Delaware and Amazon estuaries. Work also continues with five Princeton Ph.D. candidates, two in the Orinoco work, one in trace metal analysis of sediment and water, one in the soil gas study, and one in estuarine modeling.

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GROUND-WATER CHEMISTRY

CR223 TRANSURANIUM RESEARCH

TITLE: Transuranium Research

PROJECT NUMBER: CR 77-223

LOCATION: Topical Research

PROJECT CHIEF: Cleveland, Jesse M.

HEADQUARTERS OFFICE: Lakewood, CO

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 transurnaium elements (primarily plutonium) as a function of ground-water composition, pH, and redox potential.

APPROACH: Prepare synthetic ground waters with compositions similar to those in selected ground waters that were shown by previous Project studies to produce radically different speciation behavior of added plutonium. In addition, based on each of these solutions, prepare additional synthetic ground waters in which the concentrations of significant anions are individually varied over wide ranges. Determine the speciation of added plutonium in these solutions by the following procedures: (1) establish the presence of colloids by sub-micron filtration; (2) determine oxidation-state distribution of the plutonium by carrier precipitation and solvent extraction procedures: (3) for selected synthetic ground-water samples, repeat the above speciation procedures at various pH and redox potential values.

PROGRESS: A comprehensive paper, in press in the Journal of Environmental Radioactivity, consolidates speciation results for plutonium, americium, and neptunium--the three transuranium elements of most concern in nuclear waste storage--in twelve ground waters and two surface waters. The paper interprets the data from a different viewpoint and on a more rigorous scientific basis than have previous project papers, and should be a valuable contribution to knowledge of the ground-water chemistry of these three hazardous radionuclides. The paper concludes that the redox chemistry of a ground water is the single most important determinant of plutonium speciation, with water composition also being an important factor. These conclusions have been used to formulate an extensive multi-year plan for the next phase of the research program, which will explore the influence of solution composition, pH, and redox potential on plutonium speciation in synthetic ground waters.

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CR276 CLAY-WATER REACTIONS

TITLE: Geochemistry of Clay-Water Reactions

PROJECT NUMBER: CR 82-276

LOCATION: Topical Research

PROJECT CHIEF: Eberl, Dennis D.

HEADQUARTERS OFFICE: Denver, CO

PROBLEM: Clay minerals may influence the chemistry of ground water and other aqueous solutions through precipitation, dissolution, and ion-exchange reactions. An understanding of these reactions also 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 problems of predicting, enhancing, and ensuring water quality?

OBJECTIVE: (1) Develop a theory for ion exchange that would allow prediction of the exchange properties of a clay based on the 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: The Warren-Averback x-ray diffraction method was applied to the study of clay minerals, particularly to hydrothermal illites. This method has revealed that many clays react by Ostwald ripening. An understanding of this process may have far-reaching applications to the understanding of the geologic history of deposits that contain clay minerals. Experiments performed at the Ecole Normale Superieure in Paris with B. Velde have (1) led to the synthesis of illite at surface temperatures, and (2) led to the development of a new method for studying illite that is more sophisticated and better than the commonly used Kubler index. Work on a non-polluting, slow-release fertilizer continues, and the material continues to show promise.

WRD FEDERAL RESEARCH PROJECTS.....GROUND-WATER CHEMISTRY

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CR2:3 SORPTION AND PARTITION PHENOMENA

TITLE: Environmental Dynamics of Persistent Organic Compounds

PROJECT NUMBER: CR 83-283

LOCATION: Topical Research

PROJECT CHIEF: Chiou, Cary T.

HEADQUARTERS OFFICE: Arvada, CO

PROBLEM: Many persistent organic compounds are hazardous to human and ecological health. The transport characteristics of the compounds across environmental phases are strongly influenced by sorption and partition interactions with the individual phases. Quantitation 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 impact on environmental quality.

OBJECTIVE: Delineate and quantitate processes affecting the movement and distribution of persistent organic compounds in hydrogeologic systems. Specifically: (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: Initially, 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. Then, study sorption from the vapor phase in order 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-water 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: (1) A cooperative study with other geochemists in the National Research Program and in the Louisiana District was completed. The work described the distribution of haloarenes among water column, fish, and sediment in the vicinity of an industrial out fall in the Calcasieu River estuary, Louisiana. The accumulation of several chlorinated compounds by four fish species was found to closely follow the equilibrium partition pattern between fish lipid and water, as a result of rapid contaminant exchange between fish and water. In contrast, the contaminant concentration in bottom sediment was found to be much greater than the calculated equilibrium value based on concentration in water, due presumably to a poor mixing between the bottom

sediment and the bulk of water. (2) Aquifer samples from the Picatinny Arsenal site in New Jersey were characterized with respect to their moisture sorption capacities in comparison to field moisture contents. The data are being used to characterize the sorption of trichloroethylene by aquifer samples in relation to field moisture contents, a cooperative study with the New Jersey District. (3) Previous work on the solubility enhancement of organic solutes by surfactants was extended to surfactant concentrations above the critical micelle concentration. Many additional surfactants were investigated and data with a new solute (1,2,3-trichlorobenzene), in addition to DDT, were obtained. The work is still progressing. The results so far obtained show several interesting features of the solubility enhancement effect in terms of the structure of the surfactant and the micelle formed. (4) Some measurements were made on the sorption characteristics of several organic liquids from vapor phase on dry peat samples as a further test of the sorption mechanism. The observed linear isotherms and sorptive capacities are in close agreement with the partition interaction as advanced by earlier work. The results are in direct contrast to those with mineral soils where the mineral fraction shows strong adsorption of organic vapors at subsaturation humidity.

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Chiou, C. T., Kile, D. E., and Malcolm, R. L., 1988, Sorption of vapors of some organic liquids by soil humic acid and its relation to partitioning of organic compounds in soil organic matter: Environmental Science and Technology, v. 22, p. 298-303.

Smith, J. A., Witkowski, P. J., and Chiou, C. T., 1988, Partition of nonionic organic compounds in aquatic systems: Reviews of Environmental Contamination and Toxicology, v. 103, p. 127-151.

NR020 MINERAL-WATER INTERACTION IN SALINE ENVIRONMENTS

TITLE: Mineral-Water Interaction in Saline Environments

PROJECT NUMBER: NR 69-020

LOCATION: Topical Research

PROJECT CHIEF: Jones, Blair F.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: Saline hydrologic systems provide a wide range of conditions within which to examine hydrochemically-important mineral reactions, alteration or genesis, and to better 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 using 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: (1) Application of the SNORM program for diagnosis of solute origin continued. A draft of the comprehensive evaluation of saline water chemistry and solute origin for the Rustler formation aquifers overlying the Waste Isolation Pilot Project (WIPP) radioactive-waste repository site in New Mexico was completed. Such analysis is aiding the delineation of flow paths, mixing of waters, recharge, and sample contamination. The SNORM program also has been used in conjunction with non-metallic minor element data to elucidate the origin of saline solutes in the northeastern United States, Canada, and the central massif of Spain. (2) Further x-ray diffraction (XRD) results obtained for ultrafine clays in cores from the Great Salt Lake, Utah, has failed to provide added structural or secondary phase information to elucidate the detailed chemical documentation of authigenic silicate mineral reaction. Such information does seem to be emerging, however, from the XRD analysis of Madrid Basin, Spain, regional aquifer sediments. Coupled with these results, replicate major element analysis and cation exchange capacities for more than 75 samples that are less than 0.1 micron have been completed and data analysis begun. Initial response has been to undertake a major

re-evaluation of ion exchange determinative procedures, utilizing four separate solutions and concentrations on at least three suites of six samples, including reference standards. (3) In addition to solid analysis, two new flow profile-based sets (>50 each) of water samples from the Madrid Basin are being examined in detail for major and minor solutes. Initial solute association and speciation data have already been obtained for the first set. Smaller sets of water samples from the Cote Donana and Majorca, Spain, have also been analyzed under the auspices of the U.S. Geological Survey/Spain Science and Technology (S&T) Program, and the consequences for solute evolution in these areas also evaluted. All of this information is being utilized in connection with flow and mass-balance model calculations.

REPORTS PUBLISHED:

Jones, B. F., Vicente, R., and Sastre, A., 1987, Analisis normativo del agua subterranea de la depresion del Campo Aranuelo, region central Espanola: IV Symposio de Hidrogeologia, Asociasion Espanola de Hidrologia Subterranea, seccion 6, p. 919-929.

NR034 CHEMICAL CONSTITUENTS OF WATER

TITLE: Spatial Distribution of Chemical Constituents in Ground Water

PROJECT NUMBER: NR 57-034

LOCATION: Topical Research

PROJECT CHIEF: Back, William

HEADQUARTERS OFFICE: Reston, VA

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 both natural and stressed environments. This project focuses on effects of these reactions in (1) regional limestone aquifers; and (2) contaminated environments.

OBJECTIVE: Study geochemical reactions that relate to: (1) Geologic processes, including karstification, diagenesis, and ore deposition; (2) generation, migration, and attenuation of leachate components; and (3) processes of isotopic fractionation.

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. For example, (1) changes in porosity and permeability by karstification are being studied on the east coast of the Yucatan; (2) the degradation and migration of organic compounds and isotopic fractionation are being investigated at contamination sites, and in sulfide-rich ground water; and (3) comparative studies of regional systems in Ireland, Yucatan, Florida, and China are being undertaken to evaluate the environmental and geochemical consequences of hydrogeologic processes in limestone terranes.

PROGRESS: Galley proofs are now being checked on a major manuscript (1600) pages on the Hydrogeology of North America. Studies are continuing on (1) the geologic and climatic controls on the occurrence and movement of ground water in islands, and (2) the hydrogeologic controls on development of karst in tropical environments and the effects of these karst features on the hydrogeologic regime. Studies are underway evaluating the hydrogeologic controls on the development and distribution of porosity and permeability and the diagenesis of both carbonate and silicate minerals by the chemical reactions and physical processes occurring in the ground-water mixing zones.

Troester, J. W., Back, William, and Mora, S. C., 1987, Karst of the Caribbean, in Gardner, T. W., ed., Geomorphic systems of North America: Boulder, Colo., Geological Society of America, Centennial Special Volume 2.

Back, William, 1988, West Indies, in Back, William, Rosenshein, J. S., and Seaber, P. R., eds., Hydrogeology: Boulder, Colo., Geological Society of America, The Geology of North America, v. O-2.

NR041 PALEOCLIMATOLOGY AND AQUIFER GEOCHEM.

TITLE: Interface of Paleoclimatology and Aquifer Geochemistry

PROJECT NUMBER: NR 74-041

LOCATION: Topical Research

PROJECT CHIEF: Winograd, Isaac J.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: Reconstructions of continental paleoclimates of the Pleistocene Epoch have relied almost exclusively on the tree ring, packrat midden, and speleotherm records. The isotopic (denterium, oxygen-18 and carbon-13) record of old (10^3 to 10^4 year old) ground waters, and of calcitic veins marking the sites of fossil (10^5 to 10^6 year old) ground-water discharge, have not been used. Preliminary work indicates that such data will yield valuable new evidence regarding continental paleoclimate and paleohydrology of the Pleistocene and Pliocene Epochs. The data and interpretations also should 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 ground water and calcitic veins; (2) attempt correlation of inferred local variations in continental paleoclimate with global variations deduced from oceanographic studies; (3) differentiate between, and determine relative magnitude of, summer and winter recharge to major uplands receiving equal quantities of summer and winter precipitation; and (4) determine the fractionation of oxygen-18 and carbon-13 between ground waters and calcite deposits at modern springs.

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; and (3) calcitic veins and dense travertine at modern and fossil springs. Analyze water and calcite deposits for denterium, oxygen-18 and carbon-13, uranium and thorium content, and date using carbon-14, thorium-230, uranium-234/238, as appropriate. Initial work using calcite deposits will be in the southern Great Basin, where a major fossil spring-discharge area (with a modern analog, the Ash Meadows region) has been exhumed by uplift and erosion.

PROGRESS: A major interpretive report on the 250,000 year oxygen-18 climatic record from Devils Hole, Nev., was completed and submitted to Science as a lead Article. An oral report on the significance of the Devils Hole oxygen-18 time series data to the validity of the Milankovitch theory was presented at the annual meeting of the Geological Society of America (Phoenix, October 1987); the paper was very well received. An 18-inch core of vein calcite, retrieved from Devils Hole, will extend the oxygen-18 and carbon-13 record back to about 800,000 years before present.

WRD FEDERAL RESEARCH PROJECTS.....GROUND-WATER CHEMISTRY

REPORTS PUBLISHED:

Winograd, I. J., and Szabo, B. J., 1988, Water-table decline in the southcentral Great Basin during the Quaternary Period: Implications for toxic waste disposal, in: Geology and hydology of a proposed high level nuclear waste repository, M. D. Carr and J. C. Young, editors: U.S. Geological Survey Bulletin 1790 (In Press).

NR056 MODELING MINERAL-WATER REACTIONS

TITLE: Kinetic and Thermodynamic Modeling of Mineral-Water Reactions in Natural Water Systems

PROJECT NUMBER: NR 76-056

LOCATION: Topical Research

PROJECT CHIEF: Plummer, Leonard N.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: In order to model the chemical quality of ground-water systems, it is necessary to determine what reactions are occurring and their rates. Very little is known of the rates of mineral-water interaction in ground-water systems. Furthermore, little is known of the effects of variable composition on the stability of minerals, as well as the stability of metastable and amorphous phases that apparently regulate, to a large extent, the composition of certain low-temperature natural waters. Much experimental and theoretical work is needed to define the thermodynamic properties of aqueous solutions of mixed electrolytes in order to model reactions between minerals and aqueous solutions.

OBJECTIVE: Obtain experimental data on the kinetics of mineral dissolution-precipitation reactions; investigate the effects of variable composition of minerals and the stability of metastable and amorphous phases in regulating the composition of natural waters; and relate these data to modeling the chemical evolution of natural waters. Develop theory and methods for determining reaction stoichiometry and rates from observed field hydrochemical data. Apply these methods to interpret the chemical evolution of ground-water systems Develop improved thermodynamic models of aqueous solutions.

APPROACH: Study rates of dissolution and crystal growth of minerals using various methods including (1) change in weight of single crystals, (2) potentiometric and potentio-stat methods, (3) changes in solution composition, and (4) rotating disks. Investigate effects of single salts (and their mixtures) in solution on the rates. Obtain data on mineral stability from reversed solubility measurements. Use potentiometric measurements of aqueous solutions to refine thermodynamic models of aqueous solutions. Making extensive computer calculations, evaluate kinetic data, test thermodynamic models of aqueous solutions, and model the chemical evolution of ground water.

PROGRESS: A manuscript treating the thermodynamics of magnesian calcites as a ternary solid-solution system between calcite, 0.5-dolomite, and structural defects was completed. Defects caused by substitution of sulfate and sodium decrease the excess free energy of mixing in the solids. A report on the thermodynamics of strontianite-aragonite solid solutions was published. Reaction paths for dissolution of strontianite-aragonite solid-solutions in

non-stoichiometric solutions demonstrate control by stoichiometric saturation. Preliminary measurements of rhodochrosite solubility were begun and a method for removing oxygen from carbon dioxide was developed for these studies. A Guggenheim subregular excess free energy model has successfully described solid solutions in the systems $(Ca,Mg)CO_3$ $(Sr,Ca)CO_3$ $(Ba,Sr)CO_3$ and $K(Cl,Br)$. The $K(Cl,Br)$-water system was shown to attain equilibrium while solid solutions in the carbonate system initially approach stoichiometric saturation. A generalized code for examining thermodynamic properties of solid solutions (GBSSAS) was developed. The computer code PHRQPITZ for making geochemical calculations in brines was completed and documentation was prepared for technical review. The report (1) demonstrates the significance of pH scale in thermodynamic calculations with natural brines, (2) shows the necessity of maintaining an internally consistent thermodynamic data base, and (3) compiles an extensive data base of Pitzer interaction parameters. The solubility of mirabilite was measured in Great Salt Lake water and used to refine the PHRQPITZ data base for the temperature dependence of the mirabilite equilibrium constant. An interactive version of the computer code IONPIT was developed for evaluation of Pitzer interaction parameters from experimental data. A report showing that the half-life for aragonite recrystallization to calcite in fresh groundwater from the Bahamas and Bermuda is 7700 years received Director's approval for publication. A report describing the geochemical modeling and carbon-14 age dating of the Madison Limestone aquifer in parts of Montana, Wyoming and South Dakota, utilizing sulfur-34 and carbon-13 stable isotope data for the rock matrix was completed. Strontium-87 and carbon-14 data from three flow paths in the Floridan aquifer of Georgia support a hypothesis of upward leakage downgradient of the Gulf Trough structure. Detailed stratagraphic and hydrologic cross sections were prepared along the studied flow paths in the Floridan aquifer of Georgia.

REPORTS PUBLISHED:

Busby, J. F., Plummer, L. N., Lee, R. W., and Hanshaw, B. B., Geochemical evaluation of water in the Madison aquifer in parts of Montana, South Dakota and Wyoming: U.S. Geological Survey, Prof. Paper 1273-F.

Busenberg, E. and Plummer, L. N., 1986, A comparative study of the dissolution and crystal growth kinetics of calcite and aragonite: U.S. Geological Survey Bulletin 1578, F.A. Mumpton, ed., Studies in Diagenesis, p. 139-168.

Busenberg, E. and Plummer, L. N., 1987, pH measurement of low-conductivity waters: U.S. Geological Survey, Water Resources Invest. Report 87-4060, 22 p.

Plummer, L. N., and Busenberg, E., 1987, Thermodynamics of aragonite-strontianite solid solutions: Results from stoichiometric solubility at 25 and 76 degrees C: Geochim. Cosmochim. Acta, v. 51, p. 1393-1411.

NR064 ISOTOPE FRACTIONATION

TITLE: Physical Chemistry of Stable Isotope Fractionation in Hydrologic Processes

PROJECT NUMBER: NR 75-064

LOCATION: Topical Research

PROJECT CHIEF: Coplen, Tyler B.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: The stable isotopes of hydrogen, carbon, nitrogen, oxygen, silica, and sulfur show variations in their isotope abundances and may be useful in studying evaporation, ground-water mixing, 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 neither sufficiently understood nor quantified to make the most effective use of stable isotope techniques in hydrologic research.

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

APPROACH: Analyze water and mineral samples from experimental studies, from evaporating surface-water bodies, and from ground-water basins, to determine light stable isotope abundances. Relate these experimental results and field data to other measurement factors, such as relative humidity, temperature, density, and salinity, in an attempt to develop an understanding and a theoretical predictive model of the processes involved.

PROGRESS: (1) A manuscript for Science has been completed discussing the oxygen-18 (O-18) variation in a continental calcitic vein (DH-2) from Devils Hole, Nev., precipitated between 50,000 and 300,000 years before present (uranium series dates). In this cooperative study with I. Winograd, A Riggs, B. Szabo (Geologic Division), and P. Kolesar (Utah State University), comparison of the O-18 record in DH-2 with the oceanic record indicates that the last interglacial stage (marine oxygen isotope stage 5) began prior to 147,000 years before present, which is at least 17,000 years earlier than indicated by the marine O-18 record and 7,000 years earlier than indicated by the Antarctic O-18 record. This discrepancy calls for a reconsideration of oribital forcing (Milankovitch theory) as the principal cause of Pleistocene ice ages. In two cores (DH-10 and DH-11) that were recovered from Devils Hole this year, the O-18 and C-13 glacial cyclic patterns seen in DH-2

are reproduced and extend back to perhaps 700,000 years before present. (2) The collection of samples, which will be used for the determination of deuterium and O-18, has been completed for nearly 400 BENCHMARK and NASQAN sites. During the three years of sample collection, 6000 samples have been accumulated in a program designed to investigate processes affecting the spacial and seasonal distribution of deuterium and O-18 in U. S. surface waters. More than 1,000 samples have been analyzed thus far. (3) The tritium laboratory has brought three state-of-the-art liquid scintillation systems on line. The laboratory is now capable of analyzing approximately 1000 samples per year, of which half are committed to samples submitted by District offices through the Denver Central Laboratory. The backlog of network samples which comprise the base-line data for hydrological studies has been reduced to less than 2 years. (4) Isotopic analyses of Cerro Prieto geothermal system waters, Baja, Calif., in cooperation with scientists from Geologic Division, indicate continued drawdown of cooler, isotopically-lighter water from the sides and above the geothermal reservoir. (5) Analysis of samples collected during 3 years from the Catoctin, Md., and Mill Run, Va., watersheds have been completed in an effort to determine if carbon isotopes can be used to distinguish seasonably variable contributions to stream alkalinity. At Catoctin, there is a strong inverse relationship between alkalinity and C-13. The contribution from strong acid attack on calcite is nearly constant and is the major source only in the winter. During the rest of the year, calcite dissolution by biologically-derived carbonic acid is the dominant source of alkalinity. In contrast to Catoctin, at Mill Run there is a direct relationship between alkalinity and C-13 due to oxidation of methane during the rainy season when the water table fluctuates considerably. (6) In cooperation with scientists in Geologic Division, a 15 per mil range in nitrogen-15 (N-15) has been found in ammonium-bearing clays and feldspars associated with hot springs gold deposits; the compositions and field relationships are consistent with an organic source for the nitrogen. The N-15 values become more positive toward the the surface, probably due to oxygenation of the ammonium-rich fluids. (7) O-18, deuterium and tritium analyses of Madison aquifer (Mississippian Madison Limestone) and shallow ground-water samples support a conceptual model in which water, leaking from the Madison aquifer, flows along the Herren Gulch No. 2 borehole, past the deepest plug, and to the surface through faults and fissures near Greybull, Wyo. Contributions of up to 73 percent Madison aquifer water occur in shallow monitoring wells (less than 25 meters deep). This study will be prepared for District personnel as an example of the use of environmental isotopes to quantify leakage from an aquifer. (8) Preliminary in situ soil experiments with others in the NRP show that exchange with atmospheric moisture strongly affects the deuterium to hydrogen ratio (D/H) and O-18 of shallow soils. (9) In cooperation with the Agricultural Research Service, techniques for collecting and analyzing the N-15 content of residual nitrate from in situ soil column experiments have been developed. The nitrate is adsorbed on resin bags located at the base of the soil tubes. At the end of the experiment, the nitrate is extracted, condensed, and combusted. (10) Analyses of the 1986-87 storm event samples from Panola, Ga., show that only rarely does a storm have a sufficiently distinctive isotopic composition to make it possible to use D/H and O-18 as tracers of storm flow

through the watershed. Archived suites of samples from specific storms now can be analyzed. (11) Preliminary D/H and O-18 analyses from shallow ground-water samples from Blackbird State Forest, Del., show considerable temporal and spatial variation, which reflects the isotopic complication of the flow system.

REPORTS PUBLISHED:

Coplen, T. B., 1988, Normalization of oxygen and hydrogen isotope data: Chemical Geology (Isotope Geoscience Section), vol. 72, no. 4, p. 293-297.

NR093 CHEMICAL MODELS

TITLE: Chemical Models of Natural Systems

PROJECT NUMBER: NR 79-093

LOCATION: Topical Research

PROJECT CHIEF: Thorstenson, Donald C.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: The increasing need for understanding Man's impact on the chemistry of natural systems requires a continually increasing degree of sophistication in the models used to describe the processes through which this impact occurs. These 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 saturated-unsaturated interface (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: Studies of gas composition in various unsaturated-zone boreholes at Yucca Mountain (Nevada Test Site) are continuing. The sampling program is proceeding at boreholes UZ-6 (an open borehole; depth approximately 1,850 feet; cased for the upper 325 feet), UZ-6S (an open borehole adjacent to UZ-6; depth approximately 450 feet, uncased), and at UZ-1 (a stemmed borehole, instrumented--including gas sampling piezometers--at 15 levels throughout its approximately 1,200 foot depth). The sampling program has been expanded to include systematic studies of soil and/or shallow unsaturated-zone sites on Yucca Mountain and in Jackass Flats, Nevada. The gas analyses include hydrogen (by mercury-reduction detector), methane, ethane, and ethylene by methanizer-flame ionization detector gas chromatography, and the standard atmospheric gases nitrogen, oxygen, argon, and carbon dioxide. Isotopic analyses on some samples are carried out for carbon-13 and carbon-14 on the carbon dioxide, and for tritium, deuterium, and oxygen-18 on water vapor in the gas samples. Over the past year, on the order of 1,000 samples have been variously analyzed

for these constituents. After nearly four years of sampling, the carbon dioxide concentrations in UZ-1 appear to be stabilizing at levels of 0.1 to 0.15 percent in most sampling intervals; the shallowest probe (42 feet) has approximately 1.5 percent carbon dioxide, and the deepest probe (1,207 feet) shows approximately 0.3 percent carbon dioxide. Hydrogen, methane, and occasional trace amounts of ethane and ethylene are present at UZ-1. Hydrogen and methane range from approximately 0.5 ppm to approximately 3 ppm, with a vaguely defined increase with depth. In the open boreholes, which are subject to atmospheric ventilation, the concentrations of minor gases are highly variable, ranging from atmospheric concentrations during inhalation to the following concentrations during prolonged exhalation: carbon dioxide approximately 0.1 percent; methane and hydrogen 0 to approximately 0.1 ppm; ethane and ethylene undetectable. A summary of existing theory of multicomponent gas transport suggests that Fick's Laws may not be adequate to describe diffusive gas fluxes in unsaturated zones.

REPORTS PUBLISHED:

Houghton, R. L., Thorstenson, D. C., Fisher, D. W., and Groenewold, G. H., 1987, Hydrogeochemistry of the upper part of the Fort Union Group in the Gascoyne lignite strip-mining area, North Dakota: U.S. Geological Survey Professional Paper 1340, 104 p.

NR122 GROUND-WATER DISPERSION

TITLE: Dispersion of Toxic and Radioactive Wastes in Ground-Water Systems

LOCATION: Topical Research

PROJECT NUMBER: NR 81-122

PROJECT CHIEF: Wood, Warren W.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: Movement of toxic and radioactive substances in aquifer systems occur in all three phases and are controlled by both hydrologic and chemical forces. Solute movement can be greatly affected by not only physical dispersion but by other factors such as exchange sorption, chemical kinetics, and ionic distributions. Movement of gases and particulate material in the unsaturated zone are controlled by many additional parameters. 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: Many of the factors which affect dispersion can potentially be determined by laboratory tests. But the samples on which these tests are performed represent only a very small portion of an aquifer, and the results of the tests can be extremely misleading. Field methods and techniques are to be developed which will yield values of critical parameters which are regionally significant in a ground-water system.

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

PROGRESS: The origin of solutes in saline lakes on the Southern High Plains of Texas and eastern New Mexico was defined, completing the initial phase on the utilization of naturally stressed systems to evaluate dispersivity in large regional systems. The first phase of this work has demonstrated that solutes in the lakes were almost certainly derived from overland runoff and ground-water discharge from the High Plains aquifer and not from connate sea water from underlying marine Messozoic age rock, as had been proposed in the literature. Now that the origin of the solutes has been satisfactorily established, the solute phase that exists in the freshwater aquifer down gradient from these lakes can be used to gain insight into regional dispersion. Laboratory studies have been done using scanning electron microscope, x-ray, air-mill abrasion, and differential leaching time-dependent sorption studies using radioactively tagged tracers and microaudioradiography on sediments from Cape Cod, Mass., and Bordon, Ontario, Canada; tracer tests have demonstrated that matrix diffusion is a major factor in the dispersion

and transport of trace quantities of inorganic (and almost certainly organic) solutes. Matrix diffusion has been predicted from mineral analyses of tracer test data, but had not been quantitatively identified in aquifer systems. This confirmation of matrix diffusion and new methods development make possible much more precise calculation of dispersion and retardation of solutes in aquifer systems.

REPORTS PUBLISHED:

LeBlanc, D. R., Garabedian, S. P., Wood, W. W., Hess, K. M., Quadri, R. D., 1987, Natural-gradient tracer test in sand and gravel: Objective, approach, and overview of tracer movement, in U.S. Geological Survey Program on Toxic Waste--Ground-Water Contamination: Proceedings of the Third Technical Meeting, Pensacola, Fla., March 23-27, 1987, U.S. Geological Survey Open-File Report 87-109, p. B9-B12.

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Wood, W. W., and Osterkamp, W. R., 1987, Playa-lake basins on the Southern High Plains of Texas and New Mexico, Part II--A hydrological model and mass-balance arguments for their development, Bulletin, Geological Society of America, v. 99, p. 215-233.

Wood, W. W., and Fernandez, L. A., Hydrology of volcanic rocks, Ch. 39, DNAG Volume on Groundwater hydrogeology, Geological Society of America, v. O-2, p. 353-365.

Wood, W. W., and Low, W. H., Solute geochemistry of the Snake River Plain Aquifer, Idaho and eastern Oregon, U.S. Geological Survey Professional Paper 1408-D.

Wood, W. W., and Jones, B. F., Origin of solutes in saline lakes and springs on the Southern High Plains of Texas and New Mexico, in Gustavson, T. C., ed., Symposium Late Tertiary Ogallala and Quaternary Blackwater Draw Formation: Texas Bureau of Economic Geology Rept. of Investigation.

Wood, W. W., Case study: Solution and piping development of playa-lake basins on the Llano Estacado of Texas and New Mexico, Charles Higgins, ed., Chapter 3, Groundwater Geomorphology.

NR129 ORGANIC DEGRADATION

TITLE: Comparative Study of Organic Degradation in Selected Hydrogeologic Environments

PROJECT NUMBER: NR 83-129

LOCATION: Topical Research

PROJECT CHIEF: Baedecker, Mary Jo

HEADQUARTERS OFFICE: Reston, VA

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) contaminant 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. Particularly: (1) identify organic and inorganic compounds that are present as a result of the degradation of organic material; (2) study the interaction of organic compounds with soil and aquifer materials; and (3) develop geochemical models in organic-rich environments.

APPROACH: Select several organic-rich environments that have chemical and hydrologic background data and obtain samples that can be analyzed for organic and inorganic constituents. Investigate the extent and effects of chemical reactions and processes in these areas where degradative processes are primarily anearobic. Determine 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: Progress was made in three areas of investigation of the degradation of organic material in shallow aquifers: (1) Geochemical reactions were studied, in detail, along several transects in an aquifer contaminated with creosote products. Mineralogic and hydrogeologic data was combined with chemical analyses to show that the top 25 m of the aquifer are characterized by four major reaction zones and that the boundaries between these zones are, in some cases less than 1 m; (2) it was found that oil in a glacial outwash aquifer is altered by aerobic and anaerobic processes, sorption of the hydrophobic components, and volatilization. The solubilization and degradation of these compounds has greatly affected the mineralogy of the sediments and the geochemical character of the water; (3) metabolites that are intermediates in the microbial degradation of the oil were identified in ground water in the plume extending 150m downgradient from the contamination site.

WRD FEDERAL RESEARCH PROJECTS.....GROUND-WATER CHEMISTRY

REPORTS PUBLISHED:

Lindsay, S. S., and Baedecker, M. J., 1988, Determination of aqueous sulfide in contaminated and natural water using the methylene blue method, in Groundwater contamination: Field methods, ASTMSTP 963, ASTM, Pennsylvania, pp. 349-357.

NR132 WATER QUALITY AND HEALTH

TITLE: Relationship Between Chemical Quality of Natural Waters and Human Health and Disease

PROJECT NUMBER: NR 79-132

LOCATION: Topical Research

PROJECT CHIEF: Feder, Gerald L.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: In recent years, there has been increasing interest and study concerned with the possible relationships 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 both environmental and non-environmental factors. After excluding non-environmental 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 occurring in natural waters that are most likely to affect health and disease and those medical conditions most likely to be affected by water quality. Use this information to determine the temporal and spacial 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) in order 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 (USGS) and the Bureau of Vital Statistics (BVS) for both the medical and hydrologic aspects of the study. If data are lacking, collect new data in the field planned. Supplement data collection with 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. Cooperation with Dr. Howard C. Hopps, Curators Professor of Pathology, University of Missouri Medican School throughout this study.

PROGRESS: Completed initial reconnaissance and sampling in Yugoslavia. Initial analyses of ground water samples from an area where the fatal disease, Balkan Endemic Nephropathy (BEN), indicated that the water contained numerous reactive organic compounds including aniline-type compounds; the aniline-type compounds are carcinogenic, biologically active, and may play a role in BEN.

In cooperation with a nephrologist from Case Western Reserve, protocals were written and submitted to the U. S. Environmental Protection Agency (USEPA) and the U. S. Department of Agriculture (USDA) that call for extending and expanding the present studies on BEN and studying waters in Hungary and the United States to see if there is a relation betweeen very high nitrates and human health. In continuing studies on the relationships between cardiovascular disease and human health, data indicated that sodium, in the concentrations found in most ground water, does not have an important effect on cardiovascular disease mortality rates.

REPORTS PUBLISHED:

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McKnight, D. M., Feder, G. L., in press, Ecological aspects of humic substances in the environment, in MacCarthy, P., Hayes, M., Swift, R., Malcolm, R., eds., Humic Substances II: Interactions with metals, minerals, and organic chemicals: John Wiley and Sons, Chichester, England.

Feder, G. L., 1986, Hydrogeologic controls on nitrogen species in ground and surface waters: International Association of Hydrological Sciences, Publication no. 156, Proceedings of the Budapest Symposium, July 1986, p. 211-215.

Hopps, H. C., Feder, G. L., 1986, Chemical qualities of water that contribute to human health in a positive way: The Science of the Total Environment, vol. 54, p. 207-216.

Feder, G. L., 1986, Environmental influence of selenium in water of the Western United States (Perspectives): U.S. Geological Survey Yearbook, Fiscal Year 1985, p. 5-8.

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NR138 RADIOISOTOPES IN GROUND WATER

TITLE: Uranium-Thorium Series Radioisotopes in Ground-Water and Surface-Water Systems

PROJECT NUMBER: NR 82-138

LOCATION: Topical Research

PROJECT CHIEF: Kraemer, Thomas F.

HEADQUARTERS OFFICE: Reston, VA

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.

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.

APPROACH: Study uranium and thorium series radioisotopes under a variety of well known surface and subsurface conditions and relate their behavior to specific physical and chemical conditions and processes. Conduct laboratory studies, using carefully controlled conditions, to examine specific aspects of behavior. Then apply principles to hydrologic problems in less well-defined systems to see if the methods developed can contribute answers that are reasonable with respect to results from other hydrologic approaches. Apply methods to less well-constrained hydrologic problems.

PROGRESS: (1) Processed Dow No. 1 L. R. Sweezy shale samples for chlorine isotopes. Results will be the final step in determining the geological and geochemical history of this geopressured shale. (2) Completed a study of phosphogypsum disposal in the Mississippi river. Change in radium isotopes is clearly evident all the way to Venice, La. (3) Study of radioisotopes in ground water around Hayti, Mo. is largely completed Results show usefulness of uranium and radium radioisotopes in revealing cross-formational flow. (4) Study of radium in Charlotte Harbor, Fla., is largely completed. Results clearly show that the source of elevated radium in bay water is the result of ground-water influx, not phosphate mining as had been thought.

REPORTS PUBLISHED:

Kraemer, T. F., 1988, Radium content of central Mississippi Salt Basin Brines: U.S. Geological Survey Open-File Report 87-694, 10 p.

WR036 UNSATURATED ZONE SOLUTES

TITLE: Factors Determining Solute Transfer in the Unsaturated Zone

PROJECT NUMBER: WR 68-036

LOCATION: Topical Research

PROJECT CHIEF: James, Ronald V.

HEADQUARTERS OFFICE: Menlo Park, CA

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-modelling methods may not be well adapted to the situations encountered in practice. As a result, it may be impossible to assess properly the availability of a given water resource, and to predict the impact of certain human activities and of management upon such availability.

OBJECTIVE: Develop and test theories and mathematical models of reacting-solute transport to enhance the usefulness of such theories and models for assessing the impact 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: Considering the special conditions encountered in the unsaturated zone, develop new mathematical models, predicting transport of reacting solutes through porous media or at media boundaries. Use theory, numerical methods and controlled experiments. Utilize the interaction between theory and experiment for enhancing the understanding of processes involved. Stress unidirectional transport. Study water-saturated systems with slow, steady water flows and a single, essentially equilibrium-controlled chemical reaction study steady but unsaturated flows, paying special attention to the influence of water content on chemical and disperion 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 non-linear one-component chemical systems. Use existing simulation models and management models to enhance joint management and simulation capabilities.

PROGRESS: Continued interpretation of the behavior of cations during miscible displacement of solutes in unsaturated soil columns of Delhi sand. Slow elution of strontium appears to have resulted from the initial application of the strontium solution to air dry soil thus involving a process that binds the strontium ion in such a way that it is less accessable to the eluting solution. Testing of commercially available chromatography columns for theoretical behavior was continued.

WR065 SOLUTE PARTITIONING

TITLE: Partitioning of Solutes between Solid and Aqueous Phases

PROJECT NUMBER: WR 70-065

LOCATION: Topical Research

PROJECT CHIEF: Davis, James A., III

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: When solutes are introduced into a ground-water system, or into surface waters, physiochemical reactions may 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 impact 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 using 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: It was found that a combination of physical, chemical and biological processes affect the concentration of dissolved arsenic in Whitewood Creek, South Dakota, an intensively studied field site of the Surface-Water Toxics program. Algal photosynthesis induces a duirnal fluctuation in pH and a concomitant diurnal cycle in dissolved arsenic. The fluctuation in arsenic reflects the dynamic equilibrium of adsorption-desorption processes on the surface of the mineral, ferrihydrite, in response to the fluctuating pH. A study of the adsorption behavior of zinc on the surface of quartz was begun.

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Gruebel K. A. Davis J. A., and Leckie J. O. 1988. The feasibility of using sequential extraction techniques for As and Se in soils and sediments, J. Soil Science Soc. Amer. v. 52, p. 390-397.

WR080 GEOCHEMISTRY OF GEOTHERMAL SYSTEMS

TITLE: Geochemical Studies of Geothermal Systems

PROJECT NUMBER: WR 72-080

LOCATION: Topical Research

PROJECT CHIEF: Barnes, Ivan

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Geochemical data are needed for estimating reservoir temperatures, outlining favorable exploration areas, identifying potential pollution problems, and estimating recharge-discharge relations as related to depletion. Corrosion and fouling problems require such data. The carbon dioxide in the steam may be the result of (1) metamorphic reactions or (2) mantle degassing. The chemical and isotopic character of volatiles issuing from volcanoes, such as Mount St. Helens, have not been determined adequately.

OBJECTIVE: Collect and analyze gas, water, and solids for chemical, mineralogic, and isotope data to provide detailed understanding of geothermal systems in both their natural and disturbed states, and of volcanic systems before, during, and after eruptions.

APPROACH: Apply field methods developed for unstable constituents and special sample collection and preservation techniques already in use to prospective geothermal areas and to areas around Mount St. Helens and possible other volcanoes. Analyze data using present and currently developing computer programs.

PROGRESS: The lethal gas burst of Lake Nyos, Cameroon was extensively studied; all evidence to date shows that it was caused by an excessive build-up of mantle-derived carbon dioxide. Several other Cameroonian lakes were sampled and analyzed to determine any other locations where this type of natural hazard could exist. Fluids from the deep fracture zones in the Cajon Pass Drill hole were collected and analyzed for their gas, water, and isotopic compositions. Water samples from the Carson Basin and Yakima National Water Quality Assessment (NAWQA) projects were analyzed for their isotopic composition.

WR128 TRACE ELEMENT PARTITIONING

TITLE: Processes and Controls of Trace Element Partitioning in Natural Waters

PROJECT NUMBER: WR 75-128

LOCATION: Topical Research

PROJECT CHIEF: Nordstrom, Darrell K.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Development of land, water, mineral and energy resources have led to air and water-quality problems that often are caused by unhealthy mobilization of trace and radioactive elements in the environment. Trace contaminants may originate from radioactive-waste disposal, coal and base-metal mining wastes, oil-shale wastes, agricultural activities, and improper land-use development. Efforts to understand and model the trace element chemistry of natural waters are severely hampered by (1) inadequate sampling and analytical procedures, (2) inadequate or unevaluated thermodynamic and electrolyte data needed to calculate the form of dissolved chemical species and saturation states, and (3) inadequate testing of current models against laboratory measurements and well-documented field data.

OBJECTIVE: (1) Investigate methods of analyzing the species form of a trace element in a given water sample; (2) compile and critically evaluate equilibrium constants and related thermodynamic data used to make distribution of species calculations; (3) investigate the reliability of other parameters used in chemical models, especially activity coefficients; and (4) test current chemical models with carefully selected laboratory and field data to determine the range of conditions over which they can be considered reliable.

APPROACH: (1) Investigate ion-selective electrode potentiometry, ion chromatography, and high-sensitivity visible spectrophotometry for measuring specific forms of major and trace elements in natural waters; (2) search literature for thermodynamic data and evaluate for thermodynamic and statistical consistency to update the WATEQF/WATEQ2 data base; and (3) make computations with WATEQ2 under varying conditions of ionic strength, temperature, and composition of mineral solubilities to compare with laboratory and field measurements.

PROGRESS: Final papers and reports from International Stripa Project research in Sweden are being submitted. Conversion of PHAS20 computer program for evaluating thermodynamic data to a microcomputer version has been completed. Complete profiles of iron and arsenic redox chemistry in Mono Lake, Calif., have been obtained. Comparison of trace element determinations using inductively-coupled plasma (ICP), direct current plasma (DCP), graphite-furnace atomic absorption spectrometry (GFAAS) and colorimetry have been completed for a wide range of concentrations and pH.

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Ball, J. W., Nordstrom, D. K., and Zachmann, D. W., 1987, WATEQ4F--A personal computer Fortran translation of the geochemical model WATEQ2 with revised data base: U.S. Geological Survey Open-File Report 87-050, 108p.

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Nordstrom, D. K., and Parks, G. A., 1987, Solubility and stability of scorodite: Discussion; Am. Mineral., v. 72, p. 849-851.

WR139 GEOCHEMISTRY OF GEOPRESSURED SYSTEMS

TITLE: Geochemistry of Water in Fine Grained Sediments

PROJECT NUMBER: WR 76-139

LOCATION: California, Texas, Oklahoma, Louisiana

PROJECT CHIEF: Kharaka, Yousif K.

HEADQUARTERS OFFICE: Menlo Park, CA

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: (1) Study the chemistry and controls on the chemistry of water in geopressured geothermal systems; (2) provide basic data needed to identify potential pollution, waste disposal, and corrosion problems associated with extraction of energy from these systems; and (3) conduct an assessment of geopressured geothermal resources in California.

APPROACH: (1) Collect water, gas, and rock samples from prospective geopressured systems for chemical, mineralogic, and isotopic analyses; (2) collect data on sand distribution, porosity, temperature, pressure, and water salinity for assessment in California; (3) conduct membrane and water/rock interaction laboratory studies; and (4) use available and planned computer programs to analyze data.

PROGRESS: Water and gas samples were obtained using downhole samplers and from drill-stem tests, during a six month flow test at Cajon Pass' DOSECC well. Samples also were obtained from 20 groundwater and geothermal wells and springs in the area. Results show: (1) there is no mantle contribution to the volatile species; (2) water is meteoric and mainly a sodium sulfate type; and (3) there are major differences in composition of water from proximal fractures. Major additions and revisions of SOLMINEQ were made, including: (1) revision of (K) values, (2) addition of more minerals and aqueous species, and (3) addition of user defined anions, cations, and minerals.

WRD FEDERAL RESEARCH PROJECTS.....GROUND-WATER CHEMISTRY

REPORTS PUBLISHED:

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Elsheimer, H. N., Law, L. N., and Kharaka, Y. K., 1986, Methodology for the determination of iodide in saline waters with application of ion chromatography using an electrochemical detection method: Selected Papers in Hydrologic Sciences 1986, U. S. Geological Survey, Water-Supply Paper 2310, p. 65-72.

Kharaka, Y. K., 1988, Origin and evolution of water and solutes in sedimentary basins: Proc. Can-Am., Conf., on Hydrology: Hydrology of Sedimentary Basins: Application to Exploration and Exploitation, N.W.W.A., v. 3, p. 173-195.

WR165 WESTERN U.S. GEOCHEMISTRY

TITLE: Chemical and Isotope Studies of Thermal Waters of the Western United States

PROJECT NUMBER: WR 79-165

LOCATION: Western United States

PROJECT CHIEF: Mariner, Robert H.

HEADQUARTERS OFFICE: Menlo Park, CA

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 Mountian Range where the chemical geothermometers indicate much lower temperatures of water-rock equilibrium than the sulfate-isotope geothermometer and the geologic setting seem to require. This discrepancy could be due to simple mixing of thermal and fresh water 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. With this information, individual systems can be better understood and the geothermal potential of the individual thermal reservoirs estimated with greater accuracy.

APPROACH: Make 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. Although the initial area of investigation will be the Cascades of California, Oregon, and Washington, other geothermal areas in the western United States will be investigated as the project develops.

PROGRESS: Fractionation factors for carbon and oxygen isotopes in the siderite-water system were determined. Separate determinations in which iron was added to a bicarbonate-rich solution and bicrabonate was added to an iron-rich solution produced the same temperature dependent fractionation factors. This is significant because it is the first time two different reaction paths have been used to determine isotope fractionation factors for a mineral. Exactly the same method can be used for any of the carbonate minerals. Dissolved gas concentrations for waters collected at two collection

pressures from thermal wells in Boise, Idaho, were used to estimate dissolved helium concentration. Circulation times for thermal waters based on dissolved helium were virtually identical to ages calculated from radioactive carbon. Stabe isotope and gas compositions both indicate two distinct geothermal systems in the Boise area. Collection of dissolved gas at two pressures is significant because it provides a way to establish a gas distillation curve for the water of interest, circumventing Rayleigh calculations; Rayleigh distillation does not stricly apply because of the way the waters were collected. Gas samples from thermal waters of the Oregon Cascades were found to contain unusually high concentrations of nitrogen. Isotope values of the nitrogen increased as the nitrogen to argon ratio increased. The isotope composition of the nitrogen being added was found to be about plus six per mil. Similar values are often encountered in oil and gas fields.

REPORTS PUBLISHED:

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WR189 CHEMISTRY OF AQUATIC ORGANIC MATTER

TITLE: Chemistry of Aquatic Organic Matter

PROJECT NUMBER: WR 84-189

LOCATION: Topical Research

PROJECT CHIEF: Goerlitz, Donald F.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: The intrusion of industrial, agricultural, and domestically produced organic chemicals and wastes into the aquatic environment is a well-known reality and is considered to be one of the most important environmental problems. The widespread finding of these anthroprogenic 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 the field problem, in aqueous and non-aqueous conditions, sorbed, and in 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, using both on the 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 analyse; (2) do sorption studies using column technology, previously developed in this laboratory; and (3) conduct work at two field study sites on organic wood preservatives, which are ground-water contaminants, and initiate work at two other field study sites where the ground water is contaminated with crude and refined petroleum products.

PROGRESS: As a result of comprehensive organic analysis of creosote-contaminated ground water, 37 chemically and metabolically altered compounds have been identified. The compounds identified were oxidized moieties of soluble coal-tar components consisting of mainly aliphatic acids, benzoic and naphthoic acids, and additionally, aliphatic and aromatic alcohols and aromatic aldehydes and ketones. A significant number of the detected alteration products remain unidentified. The products were isolated and separated by high performance liquid chromatography (HPLC) and gas chromatography (GC) and identifications were made by mass spectrometry (MS) comparison to standards. Isolated components were introduced by GC, solid probe and HPLC thermospray. MS was performed by electron impact and chemical ionization.

WRD FEDERAL RESEARCH PROJECTS.....GROUND-WATER CHEMISTRY

REPORTS PUBLISHED:

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WR196 GEOCHEMISTRY AT MINERAL SURFACES

TITLE: Geochemical Reactions Between Water and Mineral Substrates

PROJECT NUMBER: WR 88-196

LOCATION: Topical Research

PROJECT CHIEF: White, Arthur F.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Water quality and pollution contaminantion depend strongly on geochemical processes involving reactions with mineral surfaces and substrates. Such processes include weathering reactions which contribute dissolved chemicals, sorption which removes aqueous species, and electron transfer mechanisms which 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.

APPROACH: Use methods that will define concurrent changes in mineral substrates and water during geochemical reactions in natural and contaminated aqueous systems. Use recent advances in ultra-high vacuum systems, including x-ray photoelectron spectroscopy, auger electron spectroscopy, and secondary ion mass spectroscopy, to characterize surface chemistry. Also use high-sensitivity solid state electrochemistry. Include both controlled laboratory studies and natural systems in investigations. Conduct detailed field projects to quantify the significance of mineral substrates both in controlling major element chemistry, pH, and Eh, and as sources of trace toxic components such as selenium and arsenic. Results will permit development of coupled models describing reaction kinetics and mass transport between aqueous and solid phases.

PROGRESS: Heterogeneous redox reactions at iron oxide surfaces were investigated in the presence of aqueous transition metals. The semi-conducting nature of ilmenite and magnetite permitted the fabrication of electrodes from which surface potentials and dissolution kinetics could be measured. This information, coupled with aqueous speciation data and x-ray photoelectron spectroscopy (XPS), confirmed surface reduction reactions involving ferric iron, hexavalent chromium, and pentavalent vanadium. Kinetic dissolution data indicated that the oxide surfaces dissolve linearly with time and are first order limited with respect to hydrogen activity. Initial estimates of magnetite rate constants were used to simulate the dynamic redox barrier controlling selenium mobility at the Kesterson Reservoir, Calif., using the coupled transport computer code DYNAMIX. Evaluation continued of the geologic sources of selenium (Se) in marine rocks beneath and to the west of the San Joaquin Valley of California and on the controls on Se migration at Kesterson. In field work in 1987 and 1988, in an attempt to further correlate Se occurrence in sodium and magnesium evaporite minerals with geologic unit (age) and structure, samples were collected in a drainage area above where the latest U. S. Geological Ssurvey soil survey showed the highest concentrations of Se in the San Joaquin Valley (Monocline Ridge). This area, to the south of Panoche Creek (Tumey Gulch), proved to be the area of highest mobility of Se, by at least an order of magnitude; however, only rare flood events would transport alluvial material and runoff to the valley in this inner-fan area. Values of pH in waters varied from 3.8 to 9.2, but sulfate remained the dominate anion. Se also is being determined on samples collected from potential alternative source areas, the ultrabasic intrusive rocks and/or epithermal zones of ore deposition associated with the emplacement of the New Idria Mercury Mine, an outstanding feature in the higher elevations of the Panoche Creek drainage. Thus far, analyses of pyrite, evaporites and drainage from this area, has shown no elevated levels of Se. The alluvium of the New Idria drainage (San Carlos Creek), an acidic regime, and the alluvium of the Silver Creek drainage, an alkaline regime, which both contribute to the Panoche Creek drainage, also have been sampled in detail. These samples will be analyzed not only for Se, but also for heavy metals to allow evaluation of materials available for mobilization and transport. Continued monitoring at the Kesterson Reservoir indicates that there have been significant decreases in dissolved Se after pumping ground water into the ponds. This decrease corresponds to declines in nitrate concentrations and re-establishment of reducing groundwater conditions. Studies continued on rates and mechanisms associated with surface weathering of recent basalt flows in Hawaii. XPS analyses identified high initial concentrations of an aluminum fluoride phase, formed during degassing of hydrogen fluoride on cooling. Sequential sampling over the past year demonstrated continued leaching of this phase and the progressive formation of a silica-rich surface was observed on older flows in Hawaii and Iceland. Investigations continued on the controls on water/rock interactions in the hydrothermal systems at Long Valley, Calif., and the Valles Caldera, New Mexico. Hydrothermal experiments indicated mass transfer rates of conservative species, such as chloride and boron, in the glass phase of tuffs are comparable to those predicted from mass balance calculations for the hydrothermal systems based on discharge rates and oxygen-18 data.

REPORTS PUBLISHED:

Evans, W. C., Presser, T. S., and Barnes, Ivan, 1986, Selected soda springs of Colorado and their origin: U.S. Geological Survey Water-Supply Paper 2310, Selected Papers in the Hydrologic Sciences, December 1986, p. 45-52.

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GROUND-WATER HYDROLOGY

CR090 HYDROLOGY OF LAKES

TITLE: The Role of Lakes in the Hydrologic System with Emphasis on Their Relation to Ground Water

PROJECT NUMBER: CR 74-090

LOCATION: Topical Research

PROJECT CHIEF: Winter, Thomas C.

HEADQUARTERS OFFICE: Lakewood, CO

PROBLEM: Many hydrological and geochemical processes associated with lakes are poorly understood. Characteristics of wind and vapor profiles, which are basic controls on evaporation, over lakes of various sizes in different climatic and topographic settings have been studied in detail in only a few large Western U.S. reservoirs. Many commonly used methods of estimating surface runoff to lakes are highly inaccurate. Hydrogeologic controls in seepage never have been studied adequately, either from theoretical or field perspectives. Research into these components of lake hydrology is especially critical to those responsible for lake management, protection, and restoration.

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

APPROACH: Construct theoretical and field-related mathematical models of steady-state and transient, variably-saturated ground-water conditions as related to lakes. 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, by various methods in support of the ground-water studies. Use multiple-level sensors on the lake for evaporation research purposes. Integrate chemical flux and biological studies with the hydrologic work at selected sites.

PROGRESS: (1) Extensive test drilling and well construction was done at three of the project's field sites. At Mirror Lake, N.H., two additional piezometer nests were constructed, each of which included drilling through 500 to 600 feet of crystalline bedrock. At Williams Lake, Minn., and Cottonwood Lake, N. Dak., test drilling was done to better define the geologic framework of the ground-water flow system associated with the lakes. (2) Studies evaluating the errors related to monitoring water levels with

pressure transducers and potentiometers were completed. The pressure transducers were found to drift considerably and they are unreliable for long-term monitoring. (3) Streamflow into Mirror Lake, N.H., was evaluated by comparing traditional unit-runoff estimates to actual gaged volumes. Unit runoff estimates exceeded actual discharges by a factor of 2 at high flows, and they were lower than actual discharges at low flows. This occurred despite the fact that the index watershed was quite similar to the study watersheds.

REPORTS PUBLISHED:

Winter, T. C., in press, Hydrologic studies of wetlands in the northern prairie of North America, in van der Valk, A. G., ed., Northern prairie wetlands: Ames, Iowa State University Press.

Swanson, G. A., Winter, T. C., Adomaitis, V. A., and LaBaugh, J. W., in press, Chemical characteristics of prairie lakes in south-central North Dakota: U.S. Fish and Wildlife Service Technical Report.

Winter, T. C., LaBaugh, J. W., and Rosenberry, D. O., 1988, Direct measurement of differences in hydraulic head between ground water and surface water using a hydraulic potentiomanometer: Limnology and Oceanography, v. 33, no. 5, p. 1209-1214.

Winter, T. C., and Woo, Ming-Ko, in press, Hydrology of lakes and wetlands, in Moss, M. L., Wolman, M. G., and Riggs, H. C., eds., Surface water hydrology of North America: Boulder, Colo., Geological Society of America, The Geology of North America, v. O-1.

LaBaugh, J. W., Winter, T. C., Adomaitis, V. A., and Swanson, G. A., 1987, Geohydrology and chemistry of prairie wetlands in the Cottonwood Lake area, Stutsman County, North Dakota: U.S. Geological Survey Professional Paper 1431, 26 p.

CR103 DRILLING TECHNIQUES

TITLE: Research of Drilling Techniques as Applied to Hydrologic Investigations

PROJECT NUMBER: CR 75-103

LOCATION: Nationwide

PROJECT CHIEF: Teasdale, Warren E.

HEADQUARTERS OFFICE: Lakewood, CO

PROBLEM: Many hydrologic studies need means to identify hydraulic and transport properties of porous media. Improved techniques for obtaining undisturbed and disturbed geologic samples for laboratory analyses and for conducting isolated-zone tests by use of inflatable packers are needed.

OBJECTIVE: (1) Develop methods to obtain the best quality and quantity of undisturbed cores and lithologies by experimenting with rotary-drive, stationary-piston, and hydraulic-push coring; (2) determine the most efficient use of various types of drilling muds under any drilling conditions encountered and the relation of hole size and lithologic conditions to borehole geophysical logging, using air or mud, rotary or auger drilling; and (3) determine the most efficient use of pneumatic and hydraulic packers for aquifer testing in shallow depths (1,000 ft.) and for hydrofracting or deep testing (in excess of 1,000 ft.).

APPROACH: Collect cores and samples that are adequate for laboratory analyses, and evaluate and adapt existing tools and design new ones for isolated aquifer testing. This will involve developing drilling techniques and techniques for holding drill holes open for geophysical logging, making evaluations of existing core barrels and the physical and chemical properties of drilling muds and additives according to their abilities to prevent invasion of sample material, and looking in detail at mud-rotary drilled holes. Provide consulting and advisory assistance to U.S. Geological Survey field offices. Coordinate all efforts with Borehole Geophysical Research Project. All final testing will be done in the field and all methods will have transfer value to other field projects.

PROGRESS: (1) Air-rotary drilling was conducted on the Pierre Shale research project near Hayes, S. Dak. Three wells were drilled, transducer instrumented, and grouted with neat cement. Three additional wells were drilled and instrumented with thermistors and then grouted with a neat-cement slurry. The cement curing temperature versus time were recorded. This part of the study was performed in conjunction with Steve Silliman, University of Notre Dame.

REPORTS PUBLISHED:

Morin, R. H., LeBlanc, D. R., and Teasdale, W. E., 1988, A statistical evaluation of formation disturbance produced by well-casing installation methods: Ground Water, v. 26, no. 2, p. 207-217.

CR140 BOREHOLE GEOPHYSICS

TITLE: Borehole Geophysics as Applied to Geohydrology

PROJECT NUMBER: CR 64-140

LOCATION: Topical Research

PROJECT CHIEF: Paillet, Frederick L.

HEADQUARTERS OFFICE: Lakewood, CO

PROBLEM: A large amount of geophysical data is recorded in 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, the effects of ground-water contamination, and to guide aquifer development, 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 conductivity 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) make a statistical analysis of the magnitude and sources of errors in log-derived data.

APPROACH: Log selected drill holes with core analysis, hydraulic test data, and calibration pits, and research the logs in both analog and digital form. Develop computer models to predict the behavior of gamma photons and acoustic energy in borehole environments. Compare field-log data, theoretical predictions and hydraulic tests, core analyses and test-pit values. On the basis of these comparisons, modify equipment, develop log corrections, and calculate the statistical accuracy of log data.

PROGRESS: Borehole geophysics and hydraulic tests have been used to characterize fracture permeability in several recently published studies as part of continuing research in techniques for the selection of sites for radioactive waste storage. Extensive field testing of promising new heat pulse flowmeter and acoustic sparker source logging systems have continued, and several new improvements have been incorporated into the equipment. Current research is focused on flowmeter tests during pumping and fracture interconnections identified from transient response at the start of pumping.

REPORTS PUBLISHED:

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Paillet, F. L., and Hess A. E., 1987, Geophysical well log analysis of fractured granitic rocks at Atikokan, Ontario, Canada: U.S. Geological Survey Water-Resources Investigations Report 87-4154, 36 p.

Silva, A. J., and Morin, R. H., 1987, Thermal modeling in sedimentary basins: IPF Exploration Research Conference, 1st, Carcans, France, Proceedings, June 1985, p. 289-309.

Morin, R. H., Hess, A. E., and Paillet, F. L., 1988, Determining the distribution of hydraulic conductivity in a fractured limestone aquifer, southeastern Nevada, by simultaneous injection and geophysical logging: Ground Water, v. 26, no. 5, p. 587-595.

Paillet, F. L., 1988, Fracture characterization and fracture-permeability estimation at the Underground Research Laboratory in southeastern Manitoba, Canada: Water-Resources Investigations Open-File Report, U.S. Geological Survey Water-Resources Investigations Report 88-4009, 42 p.

Morin, R. H., LeBlanc, D. R., and Teasdale, W. E., 1988, A statistical evaluation of formation disturbance produced by well-casing installation methods: Ground Water, v. 26, no. 2, p. 207-217.

CR191 SIMULATION OF SUBSURFACE-WATER FLOW

TITLE: Mathematical Simulation of Subsurface-Water Flow Using Uncertain and Incomplete Data

PROJECT NUMBER: CR 76-191

LOCATION: Topical Research

PROJECT CHIEF: Cooley, Richard L.

HEADQUARTERS OFFICE: Lakewood, CO

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 that apply to general field situations where the flow system is complex and hydrologic data are inexact are not available in general.

OBJECTIVE: (1) Reformulate, where 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 both 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 using 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 using techniques of linear and nonlinear algebra where 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) Two new methods were developed to compute exact nonlinear confidence intervals for any function of parameters derived as output from a ground-water flow model that has been manually calibrated. One method forms the confidence intervals from maximum and minimum limits of the function on a log-likelihood contour of the multivariate beta distribution of Cooley and Vecchia (1987, p. 581-599) assumed for the parameters. The other method extends the original method of Cooley and Vecchia (1987) to utilize parameter contraints imposed by the investigator. (2) A theory of parameter correlations

resulting from manual calibration shows that the fit of model-computed to observed values of dependent variables used for model calibration is more dependent on ratios of these parameters than their actual values. A simple parameter scaling technique allows the parameters that are correlated because of manual calibration to be placed in groups of ordered, scaled parameters so that the correlations may be approximated using the multivariate beta distribution. These correlations may then be incorporated into either method of computing confidence intervals. (3) A method of calculating approximate, simultaneous, nonlinear confidence intervals on hydraulic head (Cooley and Vecchia, 1987, as above) was expanded for use in numerical problems, and the accuracy of the approximate intervals was evaluated for four test cases using Monte Carlo runs. The analysis indicates that the approximate confidence intervals can be too wide to be of practical interest and that the improvements indicated above (under 1) are needed. (4) Using a first-order analysis, the hydraulic head away from a constant-head boundary of a heterogeneous porous medium has been investigated. The analysis incorporates the use of both spectral theory and Green's functions in order to allow for nonstationarity in the flow field. The variance in head obtains 90 percent of its ultimate value at six length scales away from the boundary. There appears to be a small but persistent mass imbalance with regard to the mean flow field. (5) Using a standard Lagrangian description, the variance in particle location was determined from a spectral description of the flow field in heterogeneous porous media. The analysis was completed for two extreme cases in heterogeneity (isotropic and stratified) and compared with the Borden site results. The analysis suggest that the Borden site results are best described by a stratified model.

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Hill, M. C., in press, A comparison of coupled freshwater-saltwater sharp-interface and convective-dispersive models of saltwater intrusion in a layered aquifer system: International Conference on Computational Methods in Water Resources, 7th, Boston, 1988, Proceedings.

Vecchia, A. V., in press, Estimation and model identification for continuous spatial processes: Journal of the Royal Statistical Society, Series B.

Cooley, R. L., and Vecchia, A. V., 1987, Calculation of nonlinear confidence and prediction intervals for ground-water flow models: Water Resources Bulletin, v. 23, no. 4, p. 581-599.

Vecchia, A. V., and Cooley, R. L., 1987, Simultaneous confidence and prediction intervals for nonlinear regression models with application to a groundwater flow model: Water Resources Research, v. 23, no. 7, p. 1237-1250.

CR200 UNSATURATED ZONE FIELD STUDIES

TITLE: Field Applications of Unsaturated Zone Flow Theory

PROJECT NUMBER: CR 69-200

LOCATION: Various States - in Colo., Kans., Nebr., Tex.

PROJECT CHIEF: Weeks, Edwin P.

HEADQUARTERS OFFICE: Lakewood, CO

PROBLEM: Knowledge of flow through the unsaturated zone is needed to evaluate natural recharge and return flow from irrigation, and the impact of land use changes on recharge and overland runoff. In addition, such knowledge is needed to evaluate water-management schemes involving artificial recharge and vegetation and water-table manipulation to increase water supply. Finally, unsaturated flow theory is needed to evaluate pollution hazards from surface sources. Although much research has been done on unsaturated flow phenomena, operational methods are lacking for many of the above problems.

OBJECTIVE: Develop and test methods for field measurement of hydraulic head, saturated and unsaturated hydraulic conductivity, and moisture content in the unsaturated zone. Develop and test an operational computer program for simulation of saturated-unsaturated flow phenomena on a structure-imitating basis for small-scale problems, and a more empirical watershed-type model for large-scale problems.

APPROACH: Test various methods for field determination of hydraulic parameters in the unsaturated zone at field experimental sites. Conduct experiments at these sites to test the simulation models being developed by the project staff.

PROGRESS: (1) A chamber has been designed, built, and tested for measuring evapotranspiration (ET) from small plots and individual plants. Heat and water vapor fluxes were measured at three sites on the Konza tallgrass prairie during four intensive field campaigns as part of a major NASA experiment involving about 70 ET researchers. ET data collection was continued in the San Luis valley. (2) Data continued to be collected on topographically affected gas circulation through Yucca Mountain, with updip circulation proving to be a significant component of the total flow. (3) A total of 440 soil samples were collected from the tunnel constructed beneath the waste trenches at the low-level radioactive waste site at Sheffield, Ill., to determine spatial variability at the site, and laboratory analyses have been completed. (4) Methane transport and methylotrophic consumption in the unsaturated zone has been studied and is being documented. (5) The capability to simulate solute transport in variably saturated porous media has been added to the flow computer code VS2D, and tested for varius boundary conditions.

REPORTS PUBLISHED:

Lappala, E. G., Healy, R. W., and Weeks, E. P., 1987, Documentation of computer program VS2D to solve the equations of fluid flow in variably saturated porous media: U.S. Geological Survey Water-Resources Investigations 83-4099, 273 p.

Mills, P. C., and Healy, R. W., 1987, Water and tritium movement in variably saturated glacial deposits near Sheffield, Illinois, in Proceedings of Conference on Midwestern Ground-Water Issues, Indianapolis, 1987: National Water Well Association, p. 169-186.

Healy, R. W., 1987, Simulation of trickle irrigation, an extension to the U.S. Geological Survey's Computer Program VS2D: U.S. Geological Survey Water-Resources Investigations Report 87-4086, 61 p.

Peters, C. A., and Healy, R. W., 1988, The representativeness of pore-water samples obtained with pressure-vacuum lysimeters: Ground Water Monitoring Review, v. 8, no. 2, p. 96-101.

Striegl, R. G., in press, Distribution of gases in the unsaturated zone at a low-level radioactive-waste disposal site near Sheffield, Illinois: U.S. Geological Survey Water-Resources Investigations Report 88-4025.

Kreamer, D. K., Weeks, E. P., and Thompson, G. M., 1988, A field technique to measure the tortuosity and sorption-affected porosity for gaseous diffusion of materials in the unsaturated zone with experimental results from near Barnwell, South Carolina: Water Resources Research, v. 24, no. 3, p. 331-341.

Weeks, E. P., 1987, Effects of topography on gas flow in unsaturated fractured rock--concepts and observations: Proceedings of the American Geophysical Union Symposium on Flow and Transport in Fractured Rock, p. 165-170.

Weeks, E. P., Weaver, H. L., Campbell, G. S., and Tanner, B. D., 1987, Water use by saltcedar and by replacement vegetation in the Pecos River floodplain between Acme and Artesia, New Mexico: U.S. Geological Survey Professional Paper 491-G, 33 p.

CR292 SOLUTE-TRANSPORT SIMULATION

TITLE: Ground-Water Solute-Transport Simulation

PROJECT NUMBER: CR 85-292

LOCATION: Topical Research

PROJECT CHIEF: Kipp, Kenneth L.

HEADQUARTERS OFFICE: Denver, CO

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 solute 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, 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: Work continued on the preprocessor for the heat and solute transport simulation code (HST3D). An extension of HST3D was used to investigate topographically enhanced thermal circulation of the atmosphere within Yucca Mountain, Nev., continued. It was found that inclusion of the tilt of the strata caused a second circulation path that was not present using horizontal bedding. Work began on a two-dimensional microcomputer, interactive version of HST3D (HST2DM) with graphical input and output features and

mouse-driven input. The first application will be for design and optimization studies associated with waste-heat-storage pilot plants in The Netherlands. Work has begun on coupling HST3D with a multispecies chemical equilibration calculation for application to nitrogen-compound transport. Research activities have concentrated on field and laboratory data collection and preliminary analysis of results from the Cape Cod, Mass., and the Globe, Ariz., hazardous waste field sites. More that 30,000 water samples have been analyzed for molybdenum at the Cape Cod site. Batch experiments have been completed; results show that molybdate adsorption in the aquifer should vary with changes in the local ground-water chemistry. Column experiments have been completed and data analysis is underway. Preliminary results from the column experiments indicate that molybdate adsorption is partially dependent on rate processes. The Globe, Ariz., site involves a study of acidic ground-water contamination from copper mining. One of the goals of this study is to predict when the acidic ground-water plume will reach the zone of ground-water discharge to Pinal Creek. Laboratory column experiments have been used to estimate the capacity of the alluvium to remove constituents from the acidic ground water. The principle mechanism for this removal is related to the neutralization of hydrogen ion concentration. A rise in pH causes the solubility of most metals to be exceeded and they precipitate. The unconsolidated alluvium, through which most of the plume is moving, has the capacity to neutralize approximately 1 to 2 pore volumes of acidic water. Estimates of plume breakthrough have ranged from 1 to 15 years.

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Kipp, K. L., 1987, Preliminary one-dimensional simulation of ammonium and nitrate in the Cape Cod sewage plume, in Franks, B. J., ed., U.S. Geological Survey Program on Toxic Waste-Ground-Water Contamination: Proceedings of the third technical meeting, Pensacola, Florida, March 23-27, 1987, Chapter B: U.S. Geological Survey Open-File Report 87-109, p. B-45-B-46.

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Stollenwerk, K. G., and Grove, D. B., 1987, Natural-gradient tracer test in sand and gravel: Nonconservative transport of molybdenum, in Franks, B. J., ed., U.S. Geological Survey Program on Toxic Waste-Ground-Water Contamination: Proceedings of the third technical meeting, Pensacola, Florida, March 23-27, 1987, Chapter B: U.S. Geological Survey Open-File Report 87-109, p. B-17-B-22.

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NR035 CRETACEOUS SHALE HYDROLOGY

TITLE: Hydrologic Behavior of Cretaceous Shales

PROJECT NUMBER: NR 81-035

LOCATION: Topical Research

PROJECT CHIEF: Neuzil, Christopher E.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: The nature of ground-water flow in low permeability settings is understood poorly due to (1) historic inattention to non-aquifer/reservoir 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. This information can then be exploited to extract information about flow history retained in the current conditions because of long response times and also will permit long-term prediction of 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: Pressure transducers were successfully implanted in the Pierre Shale to measure vertical differences in pore fluid pressure. The instruments are vibrating quartz type, and provide an extremely reliable measuring system. In the several months since installation, a pattern of pressures has emerged which appears to approximate predrilling conditions and indicates a naturally transient system, with a hydraulic head minimum near the center of the shale. The coupled flow experiment is continuing with consistent results indicating significant coupled fluxes. Theoretical analysis of compaction was continued to further elucidate the effects of hysteretic sediment deformation. The thermal slug test conducted previously was analyzed with excellent results; a description of the technique is in review.

NR089 SUBSURFACE TRANSPORT PHENOMENA

TITLE: Investigations of Single and Multiphase Fluid Flow, Mass and Energy Transport, and Fluid Phase Change in the Subsurface Environment

PROJECT NUMBER: NR 78-089

LOCATION: Topical Research

PROJECT CHIEF: Voss, Clifford I.

HEADQUARTERS OFFICE: Reston, VA

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 describing 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 mathematical descriptions of the system. Study system behavior using analytical and/or numerical solutions of the mathematical description, based on either hypothetical or field problem conditions. Develop simulation models and analytical methods for quantitative analysis of subsurface problems as well as novel measuring techniques as byproducts of the investigations.

PROGRESS: Theory has been developed for estimating parameter values and identifying significant processes, boundary conditions, and flow geometries for one-dimensional solute transport using field data. Optimal nework design for parameter estimation and transport model identification, based on this theory, has been successfully tested on the bromide tracer test data at Otis Air Force Base, Cape Cod, Mass. Variable-density flow and solute-transport simulation analysis have been applied to a difficult problem involving seawater intrusion with a narrow transition zone in Oahu, Hawaii, resulting in regional scale hydraulic and transport description of the aquifer. Fieldwork is underway to measure hydraulic and transport behavior at the local scale in order to investigate transition between scales.

REPORTS PUBLISHED:

Knopman, D. S., and Voss, C. I., 1987, Behavior of sensitivities in the one-dimensional advection-dispersion equation: Implications for parameter estimation and sampling design: Water Resources Research, v. 23, no. 2, p. 253-272.

Knopman, D. S., and Voss, C. I., 1988, Further comments on sensitivities, parameter estimation, and sampling design in one-dimensional analysis of solute transport in porous media: Water Resources Research, v. 24, no. 2, p. 225-238.

Lewis, F. M., Voss, C. I., and Rubin, J., 1987, Solute transport with equilibrium aqueous complexation and either sorption or ion exchange: Simulation methodology and applications: Journal of Hydrology, v. 90, p. 81-115.

Silliman, S. E., Konikow, L. F., and Voss, C. I., 1987, Laboratory investigation of longitudinal dispersion in anisotropic porous media: Water Resources Research, v. 23, no. 11, p. 2145-2151.

Souza, W. R., and Voss, C. I., 1987, Analysis of an anisotropic coastal aquifer using variable-density flow and solute transport simulation: Journal of Hydrology, v. 92, p. 17-41.

Voss, C. I., and Souza, W. R., 1987, Simulation of variable-density flow and solute transport in regional aquifers containing a narrow freshwater-saltwater transition zone: Water Resources Research, v. 23, no. 10, p. 1851-1866.

NR120 TRANSPORT MODELING--SATURATED ZONE

TITLE: Digital Modeling of Transport in the Saturated Zone

PROJECT NUMBER: NR 81-120

LOCATION: Topical Research

PROJECT CHIEF: Konikow, Leonard F.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: Management of ground-water resources requires that the extent and rate of movement of contaminants in the saturated and unsaturated zones be understood. The contaminants have been and will continue to be both accidentally and deliberately introduced into ground-water systems. Some of these contaminants constitute very hazardous conditions. Because of the immediacy of such contamination problems, understanding of the physical and chemical processes needs to be increased rapidly, and mathematical models derived from this understanding validated 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, including the unsaturated zone. Study the appropriate computer algorithms used to approximate the numerical solution to the transport equations.

APPROACH: Develop numerical models, emphasizing those ground-water systems and contaminants for which transport model needs seem most critical. This emphasis will dictate the order in which particular models are initiated. 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: Numerical simulation models were used to evaluate a number of hypotheses that could explain the evolution of the observed salinity distribution in Donana National Park, southwestern Spain. The models indicate that much of the saltwater initially in the aquifer could be flushed out by freshwater recharge about 30,000 years after the imposition of modern hydrologic stresses and boundary conditions. The salinity profile in the confining layer could be in a transient state, representing 20,000 years of change since the underlying aquifer was flushed. These best-fit times can shift by an order of magnitude because of uncertainty in the parameters of the model. Several significant improvements have been made to the method-of-characteristics solute-transport models (constant-density and variable-density versions). These include more accurate velocity interpolation schemes and more complex chemical reactions. Numerical simulation also has been used to demonstrate

the degree to which unaccounted transient changes in ground-water flow can induce erroneously high values of transverse dispersivity to be estimated.

REPORTS PUBLISHED:

Silliman, S. E., Konikow, L. F., and Voss, C. I., 1987, Laboratory investigation of longitudinal dispersion in anisotropic porous media: Water Resources Research, v. 23, no. 11, p. 2145-2151.

Konikow, L. F., 1987, AGU hydrology poster session authors polled: Eos, Transactions, American Geophysical Union, v. 68, no. 51, p. 1794.

Konikow, L. F., 1988, Present limitations and perspectives on modeling pollution problems in aquifers, in Custudio, E., Gurgui, A., and Lobo Ferreira, J. P., eds., Ground-water flow and quality modeling, NATO ASI Series, Dordrecht, Holland, Reidel Publishing Company, p. 643-664.

NR130 SURFACE GEOPHYSICS AND HYDROLOGY

TITLE: Development of Surface Geophysical Methods and Applications to Ground-Water Hydrology

PROJECT NUMBER: NR 84-130

LOCATION: Topical Research

PROJECT CHIEF: Brown, Charles E.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: Ground-water investigations require the definition of the geologic nature and hydraulic properties of media that store and transmit ground water. With recent regulations regarding ground-water contamination and disposal of toxic wastes, methods need to be calibrated for monitoring and detecting waste products and leachates around landfills and storage lagoons. Surface-geophysical methods offer a means of quickly detecting and measuring characteristics of geologic media and fluids.

OBJECTIVE: (1) Apply and extend theory and methods underlying the use of a variety of surface geophysical techniques and develop new theoretical and field models, and interpretive techniques; (2) test and demonstrate the effectiveness of geophysical techniques in practical field applications and as monitoring tools; (3) evaluate the limitations of the electromagnetic, electrical resistivity, gravity, and magnetic methods in hydrologic studies using statistical techniques and error analysis; and (4) improve existing techniques and/or devise new techniques as required.

APPROACH: Evaluate and improve existing quantitative methods and develop new techniques for analysis of hydrogeologic systems using higher mathematics, statistics, geophysical models, and carefully designed field studies. Emphasize techniques having immediate applications for needs established during current field studies. About 50 percent of this effort will be spent in the development and calibration of methods, and about 50 percent in field testing existing techniques and instrumentation and quantitatively ascertaining limitations of methods. Complete comprehensive literature survey.

PROGRESS: Ground-water quality data have been compiled into a dataset and summary statistics for chemical variables are being published.

REPORTS PUBLISHED:

Brown, C. E., in press, Determination of rock properties by borehole-geophysical and physical-testing techniques and ground-water quality and movement in the Durham Triassic Basin, North Carolina: U.S. Geological Survey Professional Paper No. 1432.

NR134 TRANSPORT IN FRACTURED ROCK

TITLE: Transport Phenomena in Fractured Rock

PROJECT NUMBER: NR 84-134

LOCATION: Topical Research

PROJECT CHIEF: Shapiro, Allen M.

HEADQUARTERS OFFICE: Reston, VA

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 that fractured formations naturally occur and have been used for various purposes by humans, 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. Because the description of fractured rock is highly dependent on scale of observation, use alternative conceptualizations of the medium in the development of these models. Investigate the parameters that arise, 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 testing of a fractured dolomite beneath a low-level, radioactive-waste disposal site was continued. The site is located southwest of Chicago, Ill., and work is being conducted in cooperation with the U.S. Geological Survey Illinois District Office. Tracer tests were conducted in a discrete horizontal fracture that is hydraulically continuous between several boreholes that are separated by more than two hundred meters. The results of the tracer tests are being used to develop mathematical interpretations of solute transport in areally extensive fractures, and to identify the transport properties associated with these models. An analysis of the tracer tests indicates that an advection-dispersion model does not accurately reproduce the experimentally observed results. Other mathematical interpretations of solute transport in areally extensive fractures are being investigated

where the transmissivity of the fracture is viewed as a spatially correlated two-dimensional random field. In a related area, research on the stochastic description of contaminant movement in heterogeneous porous media also was continued. A mathematical model that describes solute arrival time at fixed locations, using the three-dimensional stochastic properties of the porous media, was developed. The results are of importance in aiding regulatory decisions that concern solute migration in the subsurface.

NR139 GROUND-WATER QUALITY MODELING

TITLE: The Mathematical Simulation of the Transport and Reaction of Chemical Species in Ground Water

PROJECT NUMBER: NR 73-139

LOCATION: Topical Research

PROJECT CHIEF: Grove, David B.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: Mathematical techniques that describe the transport and reactions of dissolved chemical species during their flow through saturated porous media are necessary to the prediction of water-quality changes in ground water. Such predictions are necessary to allow a decision-making capability prior to possible injection of wastes as well as to provide remedial action in the case of accidental contamination of aquifers.

OBJECTIVE: Demonstrate the applicability of numerical modeling techniques to the prediction of water-quality changes during transport of solutes through the saturated ground-water systems and analyze the effects of these changes on the ground-water environment. This will provide the capability to predict the effects of chemical and physical stresses on the quality of ground water.

APPROACH: Solve the mass-transport equation through numerical means using finite difference and finite element methods and thus produce a water-quality model that will predict the effects of chemical disturbances on the ground-water system. Evaluate the effects of the disturbances on the aquifer. Involve a systems orient approach, concentrating on the use of field data and laboratory experiments to verify the model. Work closely with District, other Federal, and State research projects involved in similar studies.

PROGRESS: Analysis of field data from the Miami-Globe Ground-Water Contamination site in Arizona is continuing. Computations indicate that ground-water contaminant breakthrough into the surface water will occur within 2 to 10 years.

REPORTS PUBLISHED:

Grove, D. B., and Stollenwerk, K. G., 1987, Chemical reactions simulated by ground-water-quality models: Water Resources Bulletin, v. 23, no. 4, p. 601-615.

Grove, D. B., Stollenwerk, K. G., and Konikow, L. F., 1987, Hexavalent chromium contamination of an alluvial aquifer near Telluride, Colorado: in Proceedings of the Industrial Health Foundation Chromium Symposium, Washington, D.C., May 20-21, 1986, p. 359-377.

Stollenwerk, K. G., and Grove, D. B., 1987, Natural-gradient tracer test in sand and gravel: Nonconservative transport of molybdenum, in Franks, B. J., ed., U.S. Geological Survey Program on Toxic Waste-Ground-Water Contamination: Proceedings of the third technical meeting, Pensacola, Florida, March 23-27, 1987, Chapter B: U.S. Geological Survey Open-File Report 87-109, p. B-17-B-22.

WR024 INFILTRATION AND DRAINAGE

TITLE: Application of the Unsaturated Flow Theory to the Phenomena of Infiltration and Drainage

PROJECT NUMBER: WR 63-024

LOCATION: Topical Research

PROJECT CHIEF: Rubin, Jacob

HEADQUARTERS OFFICE: Menlo Park, CA

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

OBJECTIVE: Critically test present theories of water flow through the unsaturated porous media, and in particular, theories of infiltration and drainage. Use these theories to develop experimental techniques that will enhance studies of ground water, runoff, and other hydrologic problems in the unsaturated zone. Study unsaturated zones of various environments, especially deep unsaturated zones in the field, to measure their natural water rates, and explain these rates in terms of soil, plant, and atmospheric conditions. Use the results of such studies for the assessment of possible movement of wastes, including radioactive wastes, towards ground water.

APPROACH: Test the validity and accuracy of present predictive theories of water flow through unsaturated porous media experimentally in laboratory. Devise improved laboratory and field methods to measure such flows and to evaluate the flow-determining characteristics of soils and sediments. Use these methods and the unsaturated-flow theory for field studies of flow rates of unsaturated-zone water in settings relevant to hydrologic problems involving ground-water recharge, surface-runoff formation, or movement of radioactive and chemical pollutants.

PROGRESS: Further developed the technology needed for direct, areal determinations of the ground-water-recharging fluxes in deep unsaturated zones overlying aquifers: (1) designed, constructed and subjected to preliminary tests a waterflow-control device, which will extend the range and flexibility of the steady-state centrifuge method for swiftly and accurately determining permeabilities of unsaturated soil or sediment cores; (2) further improved this method by utilizing the previously-developed capability for measuring electrical resistance in soil cores, while they are being centrifuged; this capability speeds up and improves the method by facilitating the detection of steady-flow's onset and by making it possible to determine a core's water content and matric potential distributions during centrifugation; (3) designed, built, and started testing a sensitive touch-tensiometer to be used within

boreholes for determining matric potential profiles at depths of interest during field investigations. Continued to study the fundamental theory of unsaturated flow: (1) tested the capability of Richards equation to describe transient, unsaturated-flow during centrifuge-aided drainage of low-water-content cores, and obtained promising, though still preliminary results; (2) completed report summing up the results of the previous trapped-air studies demonstrating that air-trapping is influencing the shape of retention-curves (one of the two crucial parameters of unsaturated flow), and that it is not needed to initiate hysteresis of these curves; (3) in connection with soil-air permeability measurements, designed and successfully used an especially accurate gas flowmeter, which the U.S. Department of the Interior approved for patenting.

REPORTS PUBLISHED:

Rubin, J., Nimmo, J. R., and Hammermeister, D. P., 1987, Method and apparatus for steady-state measurement of liquid conductivity in porous media: United States Patent Number 4,679,422, granted on July 18, 1987.

Nimmo, J. R., and Akstin, K. C., 1988, Hydraulic conductivity of a sandy soil at low water content after compaction by various methods: Soil Science Society of America Journal, v. 52, no. 2, p. 303-310.

WR102 MODELING GEOTHERMAL SYSTEMS

TITLE: Modeling and Monitoring Heat and Fluid Flow in Geothermal Systems

PROJECT NUMBER: WR 73-102

LOCATION: Topical Research

PROJECT CHIEF: Sorey, Michael L.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Analysis of heat and fluid flow in geothermal systems is needed to adequately describe both 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 that obtainable from drill holes, for specific geothermal systems at Long Valley caldera (Calif.), Lassen Park (Calif.), and elsewhere. Use this information to develop realistic conceptual models of flow within these systems, both at present and in the past. 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: Numerical codes that treat single and two-phase flow in three-dimensional porous media have been obtained and modified. Numerical models of geothermal systems at Long Valley caldera and Lassen Park in California, and Grass Valley in Nevada have been used to quantify fluid and heat flow in these systems and assess their potential for energy recovery. New data from test drilling and fluid sampling obtained for the Long Valley system provide for a more realistic conceptual model. Hydrologic monitoring programs are yielding data on natural variations in geothermal systems in Long Valley and Lassen Park.

REPORTS PUBLISHED:

Farrar, C. D., Sorey, M. L., Rojstaczer, S. A., Janik, C. J., Winnett, R. L., and Clark, M. D., 1987, Hydrologic and geochemical monitoring in Long Valley caldera, Mono County, California, 1985: U.S. Geological Survey Water-Resources Investigations Report 87-4090, 71 p.

Ingebritsen, S. E., and Sorey, M. L., 1987, Conceptual models for the Lassen hydrothermal system: Bulletin of the Geothermal Resources Council, February 1987, p. 3-9.

Sorey, M. L., Farrar, C. D., and Wollenberg, H. A., eds., 1987, Proceedings of the second workshop on hydrologic and geochemical monitoring in the Long Valley caldera, July 15-17, 1986: Lawrence Berkeley Laboratory Report LBL-22852, 80 p.

Urban, T. C., Diment, W. H., and Sorey, M. L., 1987, Hydrothermal regime of the southwestern moat of the Long Valley caldera, Mono County, California, and its relation to seismicity--new evidence from the Shady Rest borehole (RDO-8): Transactions, Geothermal Resources Council, v. 11, p. 391-400.

Urban, T. C., Diment, W. H., and Sorey, M. L., 1987, Temperatures and natural gamma-ray logs obtained in 1986 from Shady Rest drill hole RDO-8, Mammoth Lakes, Mono County, California: U.S. Geological Survey Open-File Report 87-291, 100 p.

Wollenberg, H. A., Sorey, M. L., Farrar, C. D., White, A. F., Flexser, S., and Bartel, L. C., 1987, A core hole in the southwestern moat of the Long Valley caldera: early results: EOS, Transactions American Geophysical Union, v. 68, no. 20, p. 529.

WR108 GEOTHERMAL COORDINATION

TITLE: Technical Coordination and Support of WRD Geothermal Studies

PROJECT NUMBER: WR 72-108

LOCATION: Topical Research

PROJECT CHIEF: Sorey, Michael L.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Geothermal studies in the Water Resources Division are part of a nationwide research and mapping program of the U.S. Geological Survey, funded as a line item in the Geologic Division budget. These studies require planning, coordination, technical surveillance, and logistical support.

OBJECTIVE: Provide planning, technical surveillance, coordination, and logistical support services to Water Resources Division geothermal investigators.

APPROACH: Coordinator plans, arranges for staffing, approves budgets, maintains technical surveillance, and advises Chief Hydrologist through appropriate staff on the progress of the geothermal program. Coordinator reviews needs for test drilling and other logistical support as work progresses and makes necessary funds available.

PROGRESS: Geothermal research in the Water Resources Division was coordinated with that of other divisions in the U.S. Geological Survey and with that of other federal agencies. Water Resources Division research projects, treating principles, processes, and specific geothermal systems continued over a range of subject areas and in diverse geographic areas. Support was given to several projects, funded under the geothermal program, for purchase of equipment, contracts, and other miscellaneous activities.

WR121 HEAT AND MASS TRANSPORT--CASCADES

TITLE: Hydrologic Studies of Heat and Mass Transport in the Cascades

PROJECT NUMBER: WR 74-121

LOCATION: Oregon and California Cascades

PROJECT CHIEF: Ingebritsen, Steven E.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: The U.S. Geological Survey has assumed much of the responsibility for making reconnaissance surveys as a first step in the the exploration and evaluation of known geothermal resource areas. High-temperature igneous-related geothermal resources are known to exist in the Cascade Mountain Range, but the magnitude of these resources is unknown. To evaluate the most promising areas, it will be necessary to develop quantitative conceptual models of the Cascades hydrothermal systems using the information provided by concurrent geologic, geochemical, and geophysical studies.

OBJECTIVE: (1) Describe the hydrologic environments of several identified but unevaluated hydrothermal systems in the Oregon and California Cascades Mountain Range; (2) ascertain probable recharge and discharge areas; (3) determine modes and quantities of recharge and discharge; (4) interpret geologic, geochemical, and geophysical data in terms of the size, shape, and hydraulic characteristics of hydrothermal systems; and (5) use analytical and numerical modeling techniques to develop quantitative conceptual models of various systems.

APPROACH: (1) In collaboration with geologists, geochemists, and geophysicists making concurrent studies, select specific areas to be studied; (2) collect and tabulate available hydrologic data from the literature and from the files of public and private agencies; (3) supplement deficient data by field inventory, measurement, and sampling; and (4) develop quantitative conceptual models. If available modeling methods are found to be inadequate in dealing with supercritical temperatures, vapor-dominated conditions, transport in fractured media, the presence of noncondensable gases and other potentially important factors improve existing methods.

PROGRESS: A study of the north-central Oregon Cascades (approx. 44°00' to 45°15'N lat.) has involved evaluation of about 235 temperature profiles and 750 water samples. The Pliocene and Quaternary rocks that form the High Cascades comprise a large area of near-zero near-surface conductive heat flow due to meteoric recharge. In contrast, convective and conductive heat discharge is anomalously high in pre-Pliocene rocks exposed at lower elevations in adjacent parts of the Western Cascades and Deschutes Basin. If we assume that the deeper conductive heat flow beneath the High Cascades averages

100 mW m-2 (a value characteristic of areas of Quaternary volcanism), sufficient heat is swept out of the High Cascades by ground-water circulation to account for the anomalous convective and conductive heat discharge in adjacent pre-Pliocene rocks. Convective heat discharge from hot springs in pre-Pliocene rocks of the Western Cascades is an important part of the heat budget of this part of the Cascade Range. Isotopic data show that the source of these thermal waters is meteoric recharge at relatively high elevations within the High Cascades, and their chemistry indicates that they have circulated through marine rocks beneath the volcanic arc. The distribution of anomalous heat discharge in the Western Cascades, relative to Quaternary dacitic and rhyolitic volcanoes in the High Cascades, suggests that lateral flow of heated ground water into the Western Cascades is partly related to localized heat sources in the High Cascades. Therefore, there is probably significant spatial variability in deep conductive heat flow within the High Cascades. The high conductive heat flow measured in parts of the Western Cascades may be related to hydrothermal circulation. If this is the case, it is a relatively shallow-rooted phenomenon.

REPORTS PUBLISHED:

Ingebritsen, S. E., 1987, Vapor-dominated zones within hydrothermal convection systems: Proceedings of the Twelfth Workshop on Geothermal Reservoir Engineering, Stanford University, p. 291-296.

Ingebritsen, S. E., and Sorey, M. L., 1987, Conceptual models for the Lassen hydrothermal system: Geothermal Resources Council Bulletin, v. 16, no. 2, p. 3-9.

Sammel, E. A., Ingebritsen, S. E., and Mariner, R. H., 1988, The hydrothermal system at Newberry Volcano, Oregon: Journal of Geophysical Research, v. 93, no. B9, p. 10,149-10,162.

WR127 ENERGY TRANSPORT IN GROUND WATER

TITLE: Mathematical Modeling of Energy Transport in Multiphase Ground-Water Systems

PROJECT NUMBER: WR 75-127

LOCATION: Nationwide

PROJECT CHIEF: Moench, Allen F.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Subsurface formations serve as conduits, barriers, and reservoirs for water and heat energy. Meteoric water percolates through openings in the rock and exchanges heat with its environment as it moves. The physics involved in the simultaneous transfer of mass and heat in porous or fractured rock under multiphase conditions needs further study so that it can be effectively applied to the use of ground water and geothermal energy.

OBJECTIVE: Predict temperature and pressure distributions in single-phase and multiphase ground-water systems under normal and stressed conditions. Determine rates of water and heat movement in subsurface formations under natural and stressed conditions. Test equations developed for physical work.

APPROACH: Simulate field and laboratory data on transient pressure and temperature by numerical and analytical techniques. Develop and modify controlling equation to account for the physical processes that occur in earth materials. Develop models using laboratory results. Use field data for case studies.

PROGRESS: A manuscript has been prepared that proposes an exact Laplace transform solution to the problem of convergent radial dispersion. Boundary conditions use complete mass balances that account for tracer mixing with the fluid residing in the input and pumping wells. Effects of tracer mixing in the wells appear to be significant only for low porosity systems. Type curves are generated by an accurate algorithm for numerical inversion of Laplace transform solutions. Aquifer porosity and dispersivity are determined by type curve analysis of tracer breakthrough data from field sites.

WR171 HYDROLOGIC ANALYSIS OF PETROFABRICS

TITLE: Hydrologic Analysis of Petrofabrics--Sandstones

PROJECT NUMBER: WR 76-171

LOCATION: Topical Research

PROJECT CHIEF: Getzen, Rufus T.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Techniques for analyzing ground-water flow and for predicting the response of ground-water systems to natural and human-made 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 since sand-body geometry and the permeability tensor within a sand-body 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 for permeability and dispersion measurements required for adequate analyses under various conditions of stress and in various geologic settings.

PROGRESS: All of this project's manpower has been directed towards completion of a 6000-channel instrumentation/data-acquisition system (I/DAS) for use by the Nuclear Hydrology Program (NHP) in its Yucca Mountain, Nev., studies. When implemented, the NHP I/DAS will economically produce laboratory-quality hydrologic measurements in the unsaturated ground-water zone that are fully verified and documented, while operating in a hostile desert environment. Very tight environmental control for sensitive instruments, methods for in situ recalibration of non-removable sensors, completion of software design, and testing of microwave data communications have been major achievements during the year. Prototype field tests of complete systems will begin at two sites in August 1988; a third site will be added in September.

WR176 WELLS-STRAIN METERS

TITLE: Water Wells as Strain Meters

PROJECT NUMBER: WR 75-176

LOCATION: Topical Research

PROJECT CHIEF: Bredehoeft, John D.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Water wells commonly show earth-tide fluctuations. Often the magnitude of the tidal fluctuation in the well is 1 to 2 cm. 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 the strain seismometer. The problem with the water well is that other factors such as changes in barometric pressure, aquifer recharge, and pumping also can cause the water level to fluctuate. Utilizing the well for crustal strain measurements requires that we separate the strain response, the signal, from the other effects; in this case, noise. This requires careful experiments in areas where we know the crustal strain.

OBJECTIVE: To use water wells as crustal strain indicators.

APPROACH: At the present time, the U.S. Geological Survey has instrumented a set of wells along the San Andreas fault near Parkfield, Calif., for the express purpose of sensing crustal strains. The plans are to enhance the network with additional wells and improved instrumentation.

PROGRESS: The network of wells was increased in the Parkfield area where additional wells were instrumented in 1988. A total of 17 water levels at 13 locations are being monitored. At four locations, water levels are measured in both a deep and a shallow zone. Parkfield is especially interesting because a magnitude 6 earthquake is predicted to occur there in the next several years. During the past year, there have been several creep events which were observed by both water wells and nearby creepmeters. These are of interest because they demonstrate the coherence of the data.

WR178 MODELS FOR GROUND-WATER MANAGEMENT

TITLE: Models for Ground-Water Management

PROJECT NUMBER: WR 82-178

LOCATION: Topical Research

PROJECT CHIEF: Gorelick, Steven M.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Human activities influencing ground-water systems need to be properly managed. Ground-water hydraulic, solute, and thermal transport models often are used to explore aquifer management options. Generally, models are executed repeatedly under different management scenarios and the results compared. Using such an approach often avoids rigorous formulation of ground-water management objectives and fails to consider important physical and operational restrictions. It is unlikely that optimal management alternatives will be discovered using simulation techniques alone.

OBJECTIVE: Develop techniques that unify ground-water models with management-optimization methods for studying aquifer management options. Explore capabilities and limitations of various combined simulation and optimization methods.

APPROACH: Develop techniques for optimizing aquifer management by joining numerical-simulation techniques with optimization methods of mathematical programming and statistics. Develop linear management formulations amenable to the set of available optimization methods; problem linearization or decomposition may be required. Include models as constraints in the optimization models; these constraints will be in the context of other physical and operational restrictions.

PROGRESS: Work has continued on developing aquifer management computer modeling methods that account for model uncertainty. A simulation regression-management modeling methodology was developed that formulates and solves the aquifer management problem using stochastic optimization. Next, work was done on the problem of defining effective ground-water model parameter values. The issue is one of defining the meaning of flow parameters that are some spatial average of smaller-scale flow parameters. The influence of spatial variability (heterogeneity) in hydraulic conductivity, recharge, and leakage was explored. It was found that no unique averaging process defines the effective parameter values. Results from the above studies were written up and prepared for publication.

Gorelick, S. M., 1988, Incorporating assurance into groundwater quality management models, in Custodio, E., and others, eds., Groundwater flow and quality modelling: NATO ASI Series, v. 224, p. 135-150.

Wagner, B. J., and Gorelick, S. M., 1987, Optimal groundwater quality management under parameter uncertainty: Water Resources Research, v. 23, no. 7, p. 1162-1174.

Lefkoff, L. J., and Gorelick, S. M., 1987, AQMAN: Linear and quadratic programming matrix generator using two-dimensional ground-water flow simulation for aquifer management modelling: U.S. Geological Survey Water Resources Investigations Report 87-4061, 164 p.

WR179 NONISOTHERMAL MULTIPHASE FLOW

TITLE: Nonisothermal Multiphase Flow

PROJECT NUMBER: WR 82-179

LOCATION: Topical Research

PROJECT CHIEF: Herkelrath, William N.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Water plays an important role in the movement of energy and mass near the earth's surface. To describe the transport process in porous materials, the interactions between the fluid in its liquid and vapor state with the granular materials must be understood. The effects of phase change and two-phase flow upon transport processes also are important. The interactions are documented to some degree for low temperature, low pressure fluid. However, documentation at high temperatures and high pressures is needed for geothermal applications and at high temperatures for nuclear waste applications. Very little information is available.

OBJECTIVE: Determine the adequacy of the present limited description of the mechanism of transport in porous material and the various fluid-rock interactions due to temperature and pressure changes, and develop a more general and realistic model of fluid movement and mass and energy transport in porous media. Experimentally evaluate the theory of moisture movements due to temperature and pressure gradients and the effect of evaporation and condensation on the flow of moisture at elevated temperatures. Make a theoretical evaluation of various characteristics to obtain a realistic description of the transport process in the form of differential equations and to seek solutions by analytical and numerical methods.

APPROACH: Conduct experimental studies involving the use of laboratory scale models of moisture movement due to a heat source in a high temperature and high pressure environment. Use methods developed by soil physicists to measure moisture contents and pressure. Generate data to provide information on effects of absorption, evaporation, and condensation upon head and water transport. Apply fundamental laws of physics to develop equations, and solve the equations by standard numerical and analytical means. Perform limited field experiments in order to test the applicability of methodology developed in theoretical and laboratory studies.

PROGRESS: Laboratory and field investigations of multiphase, unsaturated, and immiscible flow in porous media continued. An automated time-domain reflectometry (TDR) system was developed for continuous monitoring of soil moisture content in remote field areas. This system was installed at the Hubbard Brook Experimental Forest in New Hampshire and used to study the dynamics and the spatial variability of the response of soil moisture to

rainfall events. It was found that TDR can be used to accurately measure the amount of snowmelt which reaches the soil during periods of thaw. The system also was installed at the experimental watershed at Panola Mountain, Ga., and used in a study of the dynamic response of the soil and stream chemistry to acid rain. A TDR probe was developed for measuring the volume saturation of nonpolar fluids (such as gasoline) in porous media.

REPORTS PUBLISHED:

Constantz, J. E., Herkelrath, W. N., and Murphy, Fred, 1988, Air encapsulation during infiltration: Soil Science Society of America Journal, v. 52, no. 1, p. 10-16.

WR180 UNSATURATED ZONE THEORY

TITLE: Theories of Water Flow and of Solute Transport in the Unsaturated Zone

PROJECT NUMBER: WR 82-180

LOCATION: Topical Research

PROJECT CHIEF: Rubin, Jacob

HEADQUARTERS OFFICE: Menlo Park, CA

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

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, using models that are rigorous and appropriate to analyses of solute transport in the unsaturated zone. For both water-flow and solute-transport processes, explore situations of hydrologic interest and those that may be valuable in connection with model validation or parameter determination. Experimentally test the theoretical conclusions reached in cooperation with other projects.

APPROACH: For unsaturated flow, consider model refinements dealing with 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. For solute transport, attempt to integrate the hydrodynamic dispersion approach to transport with the chemist's or ecologist's approaches to chemical equilibria, chemical kinetics, and population ecology. In addition, modify the above standard approaches to treat more realistically the special conditions encountered in natural unsaturated zones, such as the presence of two fluid phases, changes in water content, wide range of soil water fluxes, chemical heterogeneity of the porous medium. Use or adapt existing mathematical methods, especially numerical methods, and if necessary, develop new mathematical methods.

PROGRESS: As part of a search for efficient, but relatively accurate methods for solving the basic transport equations with many-component reactions, the potential of a sequential (two- or three-step) method was explored. So far, only systems with local-equilibrium-controlled reactions, unchanging phase assemblage and three-participant reaction segments have been considered, although four-participant ion-exchange segments were included. The approach used (1) made it possible to separate the solving of the partial differential and algebraic parts of the equation system; (2) ordinarily avoided the need for iteration between these two parts; (3) decreased very significantly the number of simultaneous partial differential equations to be solved; (4) made it possible to reduce considerably the total degree of the algebraic subsystem, even when the dependence of activity coefficients on ionic strength was taken into account. For the cases tested, the sequential method was applicable to all the transport cases with non-hybrid reactions (reactions with segments belonging to the same class, either homogeneous or classical heterogeneous or surface reaction class). These cases could involve any number of segments. The method also was applicable to increasingly complex, hybrid cases, all of which had a limited number of segments per reaction class. Only the simpler hybrid cases with arbitrary number of segments per class were tested. All such tests gave positive results. Two reports summing up the results of a previous study concerned with the applicability of the local chemical equilibrium assumption to solute transport analysis was completed. The reports dealt with systems influenced by precipitation-dissolution reactions, by homogeneous reactions, or by hybrid reactions.

REPORTS PUBLISHED:

Willis, C., and Rubin, J., 1987, Transport of reacting solutes subject to a moving dissolution boundary: numerical methods and solutions: Water Resources Research, v. 23, no. 8, p. 1561-1574.

WR184 HYDROLOGY OF FRACTURED ROCKS

TITLE: Hydrology of Fractured Rocks

PROJECT NUMBER: WR 83-184

LOCATION: Topical Research

PROJECT CHIEF: Hsieh, Paul A.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Understanding the process of fluid flow in fractured rocks is important to assess the suitability of underground hazardous-waste storage sites, as well as to predict waste movements if contamination occurs. Although porous-media theory provides a feasible modeling approach, the low permeability and highly heterogeneous nature of fractured rocks require extensions in current theory and field methods. It is particularly important that theoretical developments can be applied to the field on a scale that is compatible with test equipment and borehole dimensions.

OBJECTIVE: Develop a comprehensive methodology of hydraulic testing in fractured rocks, and investigate the relation between hydraulic properties measured on different scales by characterizing the heterogeneity and anisotropy of the rock mass.

APPROACH: Develop theory and application of hydraulic testing methods to determine hydraulic properties of fractured rocks. Design single-hole and cross-hole packer tests using geologic and geophysical information. Theoretically investigate the effects of scale by computer simulation using stochastic and geostatistical techniques. Using results of field tests conducted on a small scale, predict rock characteristics on a larger scale and compare the predicted results to those from large-scale tests.

PROGRESS: (1) Completed 4 months of field work at Waipahu site, Oahu, Hawaii. This included drilling eight observation wells using new drilling method, installation of multilevel packers and transducers, and running several large-scale aquifer tests to determine the horizontal and vertical hydraulic conductivities of the basalt sequences underneath the island. Test data are currently being analyzed. (2) Completed 6 weeks of field work at the Lee Valley site, San Diego County, Calif. This included cross-hole packer tests to determine the hydraulic conductivity of crystalline bedrock and its hydraulic interaction with the overlying regolith. Test data are being analyzed currently.

REPORTS PUBLISHED:

Hsieh, P. A., 1987, Characterizing the hydraulic properties of fractured rock masses: methodology and case studies, in Farmer, I. W., and others, eds., Rock mechanics: Proceedings of the 28th U.S. Symposium, Tuscon, Ariz., 1987, p. 465-472.

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Hsieh, P. A., Bredehoeft, J. D., and Rojstaczer, S. A., 1988, Response of well aquifer systems to earth tides: Problem revisited: Water Resources Research, v. 24, no. 3, p. 468-472.

WR193 TEMPERATURE EFFECTS, UNSAT. ZONE

TITLE: Temperature Effects in the Unsaturated Zone

PROJECT NUMBER: WR 87-193

LOCATION: Topical Research

PROJECT CHIEF: Constantz, James E.

HEADQUARTERS OFFICE: Menlo Park, CA

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 coeffecients 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, as well as other properties important to transport in porous materials; and (3) examine the influence of temperature upon primary hydrologic processes occurring in the unsaturated zone, such as infiltration, moisture redistribution, evaporation, and drainage.

APPROACH: Perform laboratory experiments designed to measure the temperature dependence of water retention characteristics and unsaturated hydraulic conductivities in natural porous materials, using both field cores and repacked samples. Examine relationships between the matric potential, the volumetric water content, and temperature in these materials, using experimental equipment and procedures which have been modified for high temperature. Perform field experiments to determine the influence of temperature upon water retention and transport.

PROGRESS: Extensive field and laboratory experiments were performed to demonstrate the importance of air encapsulation in the soil's transmission zone during infiltration. A new method to examine the temperature dependence of ponded infiltration was developed, and experiments at 5, 25, and 60 degrees centigrade are currently being completed for two soil materials. A method has been developed to use time domain reflectometry to measure tree moisture stress, with several field sites currently being monitored. Work on matric potential gradients in the deep unsaturated zone is still in the initial development stages.

REPORTS PUBLISHED:

Constantz, J. E., 1987, R.E. Moore and Yolo Light Clay, in Landa and Ince, eds., History of Hydrology, Gillmor (series ed.) History of Geophysics, v. 3, Washington, D.C., American Geophysical Union, p. 99-101.

Constantz, J. E., and Murphy, Fred, 1987, An automated technique for flow measurements from a mariotte reservoirs: Soil Science Society America Journal, v. 51, p. 252-254.

Constantz, J. E., Herkelrath, W. N., and Murphy, Fred, 1988, Air encapsulation during infiltration, Soil Science Society American Journal, v. 52, p. 10-16.

Constantz, J. E., in press, Distillation irrigation: A low-energy process for coupling water purification and drip irrigation: Agriculture Water Management Journal, reference no. Agwater 526.

SURFACE-WATER CHEMISTRY

CR046 ORGANIC HYDROGEOCHEMISTRY

TITLE: Origin, Characterization, and Quantification of Natural Organic Solutes in Water

PROJECT NUMBER: CR 68-046

LOCATION: Topical Research

PROJECT CHIEF: Malcolm, Ronald L.

HEADQUARTERS OFFICE: Arvada, CO

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

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) understand 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 effect of natural organic solutes in water purification: reverse osmosis, chlorination, activated charcoal, and ozonation.

APPROACH: (1) Conduct intensive stream sampling of the Yampa, Ohio, Missouri, and Ogeechee Rivers to determine climatic, geologic, and seasonal variations in natural organic substances; (2) characterize organic matter from water, soils, and plants in wetland environments to determine origin and source; (3) cooperate with other researchers and District personnel in programs that emphase organic-contaminant movement in ground water; and (4) predict the amount and variety of chlorinated compounds in water from the characterization of natural organic matter.

PROGRESS: Basic research on humic substances in rivers, lakes, ground waters, and the ocean has been fruitful. The characterizations of lake humic substances from Fremont and New Fork Lakes (Wyoming) are complete except for carbon-14 aging and carbon-13 (C-13) determinations. C-13 nuclear magnetic resonance (NMR) spectroscopy is the most definitive characterization tool. In these pristine oligotrophic lakes, only small compositional differences in humic substances are exhibited with depth or source of the humic substances. The characterization of ocean humic substances are almost complete. These humic substances are exceptionally low in armaticity (14 percent or less) and have a carbon distribution, as shown by C-13 NMR spectroscopy, to be similar to stream humic substances, but their C-13 values of -22 or less are very different from the -30 of stream humic substances. The source of dissolved

marine humic substances is still in question. There has been considerable application of our research on humic substances to general geochemistry. The solid-state C-13 NMR spectra of humic and fulvic acids from stream, peat, soil, ground water, and ocean environments are distinctive and different with a few commonalities. Therefore, it has been concluded that soil humic substances are not the primary source of stream humic substances and the humification process in soils is different from that in aqueous environments.

REPORTS PUBLISHED:

Chiou, C. T., Kile, D. E., Malcolm, R. L., and Leenheer, J. A., 1987, A comparison of water solubility enhancement of organic solutes by aquatic humic substances and commercial humic acids: Environmental Science and Technology, v. 21, p. 1231-1234.

Vassalo, A. M., Wilson, M. A., Collins, P. J., Oades, J. M., and Malcolm, R. L., 1987, Structural analysis of geochemical samples by solid state nuclear magnetic resonance spectroscopy: I. Role of paramagnetic material: Analytical Chemistry, v. 59, p. 558-562.

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Chiou, C. T., Kile, D. E., and Malcolm, R. L., 1988, Sorption of vapors of some organic liquids on soil humic acids and its relation to partitioning of organic compounds in soil organic matter: Environmental Science and Technology, v. 22, p. 298-303.

Sarkar, J. M., Malcolm, R. L., and Bollag, J. M., in press, Enzymatic coupling of 2, 3-dichlorophenol to stream fulvic acid in the presence of oxidoreductases: Soil Science America Journal, v. 52, p. 770-774.

CR132 ORGANIC POLYELECTROLYTES

TITLE: Behavior of Natural Polyelectrolytes in Water

PROJECT NUMBER: CR 68-132

LOCATION: Topical Research

PROJECT CHIEF: Wershaw, Robert L.

HEADQUARTERS OFFICE: Arvada, CO

PROBLEM: Natural organic polyelectrolytes are highly active materials that are present in practically all natural water systems. They interact with both 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. Both 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; (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 types of chemical compounds that result from the chlorination of natural polyelectrolytes; (5) characterization of the effect of organic polyelectrolytes on the chemical speciation of major cations (sodium, calcium, and potassium) and trace metals (copper and iron) in water; (6) development of nuclear magnetic resonance (NMR) spectroscopy methods for the characterization of humic materials; (7) determination and characterization of organic pollutants in ground water and precipitation; (8) characterization of the interaction of organic pollutants from precipitation with soil systems; (9) investigation of various substrates for sample introduction; and (10) characterization of NMR spectra obtained for various compound functionalities.

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 spectroscopy; (3) use carefully characterized organic polyelectrolyte fractions in experiments designed to elucidate the sorption and solubilization reaction

of pollutants and nutrients with natural organic polyelectrolytes; (4) characterize behavior of aquatic fulvic acid as an electrolyte by potentiometric titration; (5) characterize effect of fulvic acid on activity of Na, K, and Ca by dialysis and specific ion electrode measurements; (6) characterize effect of major cations on the complexation of Cu by fulvic acid, using potentiometric titrations to measure cupric ion activity and using ultraviolet (UV) titrations to measure absorbance of the charge transfer band associated with the Cu-fulvic acid complex; (7) evaluate the effect of fulvic acid on the activities of major cations and trace metals in different aquatic environments by chemical equilibria calculations and analysis of field samples; (8) isolate organic pollutants from water systems.

PROGRESS: A cooperative study was begun with the College of Agriculture of the Hebrew University of Jerusalem in Rehovot, Israel. Humic and fulvic acids were extracted from grape marc and manure composts of different ages. The humic acids were fractionated dextran gels (Sephadex) and the C-13 NMR spectra of these fractions were measured. These samples provide a unique opportunity to follow the formation of humic substances under controlled conditions. Comparison of the spectra of the fractions before and after composting should allow us to determine what chemical changes take place during the humification process. Preliminary results indicate that NMR spectra of the fractions from fresh grape marc and manure are very similar to the spectra of the corresponding fractions from well-composted materials. However, the relative concentrations of the fractions are different in the well-composted materials from those in the fresh materials. (2) A collaborative study on the use of lanthanide shift reagents to help in the assignment of the chemical shifts in the NMR spectra of humic acid fractions has been initiated with Dr. Michael Mikita of the University of Colorado, Denver Center. Preliminary results have not been very promising because the lanthanide reagents cause the humic fractions to precipitate. However, it may be possible to measure the solid-state NMR spectra of these precipitates. (3) A study of humic acids from the Philippines has been undertaken in collaboration with scientists from the University of the Philippines. Humic acids from a peat soil, an agricultural soil, and a lake sediment from the Philippines were fractionated by sorption chromatography on cross-linked dextran gels (Sephadex). The NMR spectra of these fractions have sharp, well-resolved bands which can be attributed to lignin-like structures, carbohydrates, and aliphatic groups. (4) A second sampling of the dissolved organic acids present in the plume downgradient of the oil spill at Bemidji, Minn., was carried out and the samples have been characterized by solution-state C-13 NMR spectroscopy to determine changes in the organic composition of the plume. This work is part of a continuing study on the role of organic acids in the geochemistry of this contaminated aquifer. The hydrophobic neutral fraction from the Bemidji ground water has also been isolated and characterized by NMR spectroscopy. (5) In connection with the work at the Bemidji site, a sample of the humic substances from an uncontaminated well was collected. This sample will be used to study the role of humic substances in the chemical processes of ground-water systems. (6) "Endmember" aquatic fulvic acid samples were collected from two lakes in the Dry Valley region of Antarctica. These lakes

have no terrestrial inputs of carbon compounds; therefore, the fulvic acids must arise solely from micro-organisms (mainly algae) growing in the lakes. These samples are currently being characterized. (7) Samples of humic substances from the Yakima River in Washington were collected to determine the effects of agricultural practices on the chemistry of humic substances in surface water. This work was carried out in conjunction with Diane McKnight (NRP) and Stewart McKenzie of the Portland office. (8) A study has been initiated to develop a procedure for the preparation of the trimethylsilyl ethers and esters of humic substances. The C-13 and Si-29 NMR spectroscopy of these derivatives will be used to determine the concentrations of hydroxyl and carboxyl groups in humic substances. Preliminary results indicated that we have been able to develop a worthwhile procedure. Several different NMR pulse sequences have been used to obtain as much chemical structural information as possible from the samples. (9) In cooperation with the Organic Geochemistry project, liquid state NMR spectroscopy was used to characterize the International Humic Substance Society's (IHSS) standard and reference humic substance samples; quantitative NMR spectra of the samples have been measured and an open-file report is being prepared.

REPORTS PUBLISHED:

Aiken, G. R., Brown, P. A., Noyes, T. I., and Pinckney, D. J., in press, Molecular size and weight of fulvic and humic acids from the Suwannee River: U.S. Geological Survey Open-File Report 87-695.

Aiken, G. R., Thorn, K. A., and Brooks, M. H., 1987, Nonvolatile organic acids in ground water contaminated with crude oil: U.S. Geological Survey Program on Toxic Waste-Ground-Water Contamination: Proceedings of the third technical meeting, Pensacola, Florida, March 23-27, 1987: U.S. Geological Survey Open-File Report 87-109, p. 631-632.

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Earl, W. L., Wershaw, R. L., and Thorn, K. A., 1987, The use of variable temperature and magic angle spinning in studies of fulvic acids: Journal of Magnetic Resonance, v. 74, p. 264-274.

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Thorn, K. A., Steelink, Cornelius, and Wershaw, R. L., 1987, Methylation patterns of aquatic humic sublstances determined by C-13 NMR spectroscopy: Organic Geochemistry, v. 11, p. 128-137.

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CR189 GEOCHEMICAL KINETICS STUDIES

TITLE: Geochemical Kinetics Studies of Silicate Rock Hydrologic Systems

PROJECT NUMBER: CR 75-189

PROJECT CHIEF: Claassen, Hans C.

HEADQUARTERS OFFICE: Lakewood, CO

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. Combining solution chemistry and the results of surface-alteration studies, suggest reaction models.

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. These measurements will allow the relations between variations in input (recharge) and output (discharge) water quality to be described and will aid in design of controlled laboratory experiments, and the results of these laboratory experiments will provide data for kinetic mechanism elucidation. In addition to studies of the aqueous phase, describe changes that occur in the solid phase, using instrumental (nondestructive) and chemical-analytical techniques.

PROGRESS: Collection and analysis of water vapor samples from field sites continued in order to test the following hypotheses: (1) air moisture is in approximate isotopic equilibrium with precipitation in the near-earth surface environment at a Rocky Mountain watershed; (2) the isotopic composition of air moisture determines the observed summer enrichment in soil moisture; (3) isotopic composition of precipitation quantitatively determines near-earth surface climate variables of temperature and humidity. Areal distribution of chloride-ion deposition in the Western United States correlates to important hydrologic variables further supporting the hypothesis that ground-water chloride ion concentration may quantitatively relate to effective moisture in many watersheds. The foregoing hypotheses continue to

be tested in contemporary watersheds and may be used to determine climates associated with paleowaters. The question of dry-deposition of chloride continues to be addressed.

CR199 CHEMISTRY OF SEDIMENT SURFACES

TITLE: Water Chemistry of Sediment Surface Coatings

PROJECT NUMBER: CR 76-199

LOCATION: Topical Research

PROJECT CHIEF: Goldberg, Marvin C.

HEADQUARTERS OFFICE: Lakewood, CO

PROBLEM: Local chemical composition of natural waters is heavily influenced by sediment surface reactions. Because of sorption phenomena on sediment surfaces, sediments carry larger concentrations of many materials, such as trace metals, pesticides, and salts than water does. The sorbed species may move in either direction across the solid-liquid interface in response to changes in chemical potential set up on either side of the interface. Sediment 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, the variety of reactions that govern the distribution of chemical species between the solid and liquid phases must be understood. The solid phase acquires coatings as a consequence of its prior reactive history; these coatings are an important characteristic in determining the current surface chemical reactivity. An understanding of the coating process, chemical composition of the coating, and chemical reactivity of the coatings when exposed to various bulk water compositions is a prerequisite for definition, prediction, and perhaps manipulation 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; and (3) examine the chemical processes by which sediment coatings are formed and determine the nature of the bonding between coatings and sediment surfaces.

APPROACH: Use spectroscopic methods, mainly Fourier transform infrared spectoscopy, Laser Ramam spectroscopy, and three-dimensional fluorescence spectroscopy, to determine the surface chemical composition of natural and prepared sediment coatings. Obtain supplemental information on the surface composition with Auger and Low Electron Excitation spectroscopy. Examine a natural sediment-water system containing Gibbsite or Geothite type coatings. Simultaneously, synthesize laboratory coatings of the same materials. Study the sorption reactions of materials to understand the surface-bonding mechanism of the coating and of the sorbing material, the surface chemical reactivity to these species, and the speciation of each sorbed component. Characterize fluorescence organic surface coatings and micelles in natural water samples to evaluate the sorption influence of these materials on local

water composition. Conduct studies jointly with the Louisiana District and other research projects to obtain information needed to define the role of some of the bottom coatings on the uptake and release of elements held on the sediment surfaces in Lake Bruin, to use three-dimensional fluorescence spectroscopy to characterize natural organic coatings as an aid in understanding very low dissolved solute waters, and to use three-dimensional fluoresecence spectroscopy to obtain definitive information on humic acid fraction patterns and augment studies of the formation of charge-transfer complexes.

PROGRESS: Photolysis studies have been conducted on organic molecules that contain the reactive groups carboxylates, glycols, aldehydes, and amino acids. Organic molecules with these reactive groups are more prevalent in water due to their increased solubility compared to organic species. These molecules will photolyze when adsorbed to a photolytically reactive surface such as iron, manganese, titanium, or other transition series elements. Because iron and manganese are the most likely to occur in natural waters, studies have focused on iron substrates. Photolysis in these systems was found to result in a reduction of charge of both crystalline and amorphous iron from Fe(3+) to Fe(2+) and simultaneously the degradation of the organic adsorbate molecules, usually by oxidation. New findings reveal that the photolysis of goethite with adsorbed benzoate results in Fe(2+) and a hydroxyl radical (.OH). The production of .OH in natural waters by this reaction has not been proven heretofore; its existence was substantiated by measuring salicylate which is the reaction product of .OH and benzoate. The reaction taking place are:

$$Fe(III){:}OOCR + light \longrightarrow Fe(2+) + .RCOO$$
$$Fe(2+) + H+ \longrightarrow Fe(3+) + .OH + OH-$$

.OH is a very reactive radical intermediate that is capable of oxidizing other molecules in the immediate area and its production from these photolytic systems has not been recognized previously. When the adsorbates on goethite of the amino acids, glycine and alanine are photolyzed, the overall reaction products are Fe(2+) and formaldehyde from the glycine adsorbate, and Fe(2+) and acetaldehyde from the alanine adsorbate. The reaction products are pH dependent with more reaction product formed as the solution becomes more protic. The product concentrations are nonlinear as a function of time for Fe(2+) and linear for formaldehyde and acetaldehyde production. A kinetic model containing rate equations for all the possible reaction intermediates of the amino acid photolysis reaction was developed. Analysis of the reaction, with the aid of the kinetic model, allowed selection of the rate determining reactions; out of 72 possible rate equations, it was determined that 17 were adequate to describe the reaction. The model demonstrated that five intermediate radical species play a leading role in the reaction; these species were .OH, HCO_3, HO_2, O_2^-, and CO_3^-. Of these, only carbonate radicals change concentrations as a function of reaction time. The decrease in carbonate radical concentrations correlate with the accumulated increase in Fe(2+) produced in solution. This indicates that carbonates play a leading

role in aquatic photolysis, acting as radical scavengers of other steady-state radical intermediates. Because carbonates are prevalent in most natural waters, it is important to recognize their effect on natural photolysis. Chlorinated organic materials in surface waters lose chlorine photolytically through the reaction:

$$Ar\text{-}Cl \text{ -----> } .Ar + Cl^-$$

The chemical requirements for this reaction to take place were found to exist in the sediments of the Calcasieu River, La. Two materials, octachlorostyrene and octachloronapthalene, are photolytically dechlorinated in this river, fairly rapidly. It was determined that octachlorostyrene has a half life of 1 to 2 days in normal sunlight. Its quantum yield is 2.2 x 10E-2 moles of chlorine per Einstein of photons adsorbed. Octachloronapthalene has a half life of 2 to 3 days in normal sunlight and has a quantum yield of 8.6 x 10E-5 moles of chlorine per Einstein of adsorbed photons. An index method to categorize any given surface water in terms of abiotic photoactivity was developed based on measuring the steady-state concentration of .OH. Laboratory and field methods used n-butyl chloride as the .OH trap. Measurements of local waters including the Chatfield Reservoir, Colo., and the Platte River, Colo., showed steady-state .OH concentrations from 10E-16 to 10E-17 moles/liter. Measurements in the upper Arkansas River, Colo., indicated large amounts of photoactivity due to the presence of relatively large amounts of iron. The steady-state .OH concentrations were proportional to the concentrations of dissolved iron. Steady-state .OH concentrations ranged from 1.3 x 10E-10 moles of .OH/gram of Fe to 2.5 x 10E-11 moles of .OH/grams of dissolved Fe. Excitation, Emission Matrix (EEM) fluorescence patterns of natural waters were found to be sufficiently descriptive and selective to allow characterization of the waters as to type, organic content, and changes in this content along a watercourse. Measurements were made of the fluorescence EEM matrixes of several waters in Colorado. The EEM matrix patterns at different locations on the Platte River and on samples collected from other sites were matched to each other and to standard materials normally found in surface waters. It was possible to characterize the organic materials in the Platte River at six different sites along the watercourse by this technique. Results to date indicate this method can be useful for tracking flow of natural organic solutes and for examining the organic partition between sediment and water phases if organic constituents in the system fluoresce (true for about 90 percent of the organic species). It is a nondestructive technique that requires no unusual sample handling; all samples are left in the natural state prior to and during the collection of the EEM matrix.

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CR207 ARID REGIONS CLIMATE AND CHEMISTRY

TITLE: Arid Regions Climate and Chemistry

PROJECT NUMBER: CR 77-207

LOCATION: Southern Nevada (Nevada Test Site)

PROJECT CHIEF: Benson, Larry V.

HEADQUARTERS OFFICE: Lakewood, CO

PROBLEM: Few guidelines have been established for the quantitative characterization of past climates using data obtained from paleolacustrine 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 oxygen-18 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 in inorganic-sediment) from lake-sediment cores in order to establish time-series records of climate; (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 and 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) evaluate mesoscale model of Great Basin climate being developed at the National Center for Atmospheric Research using generalized surface-hydrology model of the Lahontan basin (model combines precipitation-runoff, lake evaporation, and lake thermal-evolution models); (6) Apply mesoscale calculations and generalized surface-hydrology model to determine the type of climate responsible for Pleistocene highstand lakes.

PROGRESS: North shore of Pyramid Lake, Nev., was cored to a depth of 75 m. Magnetic susceptibility measurements completed. Sedimentology on 20 percent of the core completed. Subsampling of core is 10 percent complete. Samples for radiocarbon and tephrochronology submitted for analysis. The Truckee River surface-water system is being monitored for change in oxygen-18 content. Five weather stations, two radiation stations, four thermister stations, and transducer (lake level) station established in the Pyramid Lake area.

REPORTS PUBLISHED:

Benson, L. V., and Thompson, R. S., 1987, Lake-level variation in the Lahontan basin for the past 50,000 years: Quaternary Research, v. 28, p. 69-85.

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CR278 ORGANIC CONTAMINANTS AND WATER QUALITY

TITLE: Origin, Fate, and Transport of Organic Compounds in Surface and Ground Waters and their Effect on Water Quality

PROJECT NUMBER: CR 83-278

LOCATION: Topical Research

PROJECT CHIEF: Pereira, Wilfred E.

HEADQUARTERS OFFICE: Arvada, CO

PROBLEM: Organic material associated with river and stream sediments and aquifer porous media plays a major role in sorption, chemical alteration, desorption, and transport of anthropogenic organic compounds. Inadequate knowledge of the nature and role of organic carbon residing on suspended particulates, bed sediments, and aquifer porous media continues to hamper interpretive water-quality investigations. The problem is further compounded by the complex physiochemical behavior of organic compounds and a lack of knowledge of fundamental processes governing their fate and transport in rivers, streams, and contaminated aquifers.

OBJECTIVE: (1) Determine physiochemical and biological processes, controlling the fate and movement of organic compounds associated with suspended sediments, bed material, and aquifer porous media; (2) determine the nature and role of organic carbon associated with suspended and bed sediment and aquifer porous media; (3) determine bioavailability of organic contaminants to stream biota.

APPROACH: (1) Collect suspended sediment, bed material, and biota from the Mississippi River and Calcasieu River, La.; (2) characterize and quantify the organic compounds associated with the biota, sediments, and water, using tandem-mass spectrometry; (3) investigate fate and movement of selected organic pollutants in suspended and bed sediment; (4) investigate physical, chemical, and biological processes taking place at the sediment/water interface; (5) study fate and movement of agricultural chemicals in the Mississippi River and its tributaries.

PROGRESS: Geochemical studies were conducted to better understand the movement and fate of polynuclear-azaheterocyclic compounds, or azaarenes, in aquifers contaminated by wood-treatment chemicals. Two- and three-ring azaarenes and their oxygenated and methylated derivatives were identified in ground water by gas chromatography-mass spectrometry. The presence of oxygenated azaarenes in anaerobic zones of ground water suggested that these compounds probably were microbial-transformation products. Laboratory anaerobic-degradation studies were designed to investigate metabolic pathways of azaarenes. Microbial metabolic-transformation products of quinoline, isoquinoline, and 4-methylquinoline identified in laboratory anaerobic

cultures were identical to those detected in contaminated ground water at two hazardous waste sites. Microbial N-, C-, and O-methylation reactions were reported for the first time and partial metabolic pathways were elucidated. Distributions of azaarenes in anaerobic zones of ground water indicated that two-ring azaarenes are degraded by indigeneous micro-organisms. Oxygenated derivatives of azaarenes are more water soluble, mobile, and biorefractory than parent azaarenes; hence, they are more persistent in contaminated aquifers. Several publications resulted. Mechanistic studies using water enriched with oxygen-18 demonstrated that under aerobic and anaerobic conditions, the oxygen atom of water is enzymatically incorporated as hydroxyl into the quinoline molecule. Haloarenes derived from anthropogenic activities were identified and quantitated in bed sediments of the Calcasieu River. In waters of high salinity and conductivity, the water solubility of these compounds is decreased and hence their partition coefficients are significantly increased, resulting in a "salting-out" effect. Therefore, these sediments serve as a major sink for the haloarenes. The "salting-out" effect observed for the haloarenes indicates the importance of estuarine sediments in determining the geochemical transport and fate of hydrophobic organic pollutants. Studies of distributions of halogenated organic compounds in different compartments of the Calcasieu River estuary (biota, bottom, suspended sediments, and the water column) suggested that contaminant distributions in biota, suspended sediments, and the water column were closer to equilibrium than contaminant distributions between biota, bottom sediments, and the water column. Bioconcentration factors were determined and found to be in reasonable agreement with literature values. Equilibrium distribution patterns provide a useful basis for assessing the impact of system dynamics on fate and transport of halogenated organic compounds in estuarine systems. Studies conducted on the lower Mississippi River and its tributaries have shown that this 1,200-mile river reach is contaminated by agricultural chemicals (herbicides and chlorinated pesticides) and their degradation products. Transport calculations indicate that about 100 metric tons of atrazine are discharged into the Gulf of Mexico every year. Chlorinated pesticides are bioconcentrated in catfish. New technology was developed for the determination of contaminants at concentrations less than a ug/L using gas chromatography (GC)-Ion Trap Mass Spectrometry and GC-Tandem Mass Spectrometry.

REPORTS PUBLISHED:

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Pereira, W. E., Rostad, C. E., Updegraff, D. M., Bennett, J. L., 1988, Microbial transformations of azaarenes in creosote contaminated soil and ground water: Laboratory and field studies: Proceedings of the International Conference on Water and Wastewater Microbiology, Newport Beach, Calif., February 8-11, 1988, v. I, p. 5-1-5-7.

Pereira, W. E., Rostad, C. E., Leiker, T. J., Updegraff, D. M., Bennett, J. L., 1988, Microbial hydroxylation of quinoline in contaminated ground water: Evidence for incorporation of the oxygen atom of water: Applied and Environmental Microbiology, v. 54, no. 3, p. 827-829.

CR282 ANALYTICAL CHEMISTRY OF INORGANICS

TITLE: Research in the Analytical Determination of Inorganic Constituents in Water and Water Related Materials

PROJECT NUMBER: CR 83-282

LOCATION: Topical Research

PROJECT CHIEF: Taylor, Howard E.

HEADQUARTERS OFFICE: Arvada, CO

PROBLEM: The determination of inorganic constituents in water and water-related materials (that is, suspended matter, bottom sediment, etc.) in a sensitive, accurate, and efficient manner requires highly sophisticated analytical methods and plays a significant role in the study of water quality and environmental chemistry. These methods employ instrumentation based on physical and chemical properties and phenomena. The solution of analysis problems (sensitivity, selectivity, interference effects, data collection/reduction, and system automation) often requires the design and construction of suitable laboratory and field instrumentation and apparatus. The study of specialized analytical problems, such as chemical speciation, also requires unique approaches. In addition, the adaptation of analytical chemistry technology to the solution of specific environmental chemistry and water quality hydrologically related problems requires an extensive research and development effort both in the laboratory and the field.

OBJECTIVE: (1) Investigate new concepts and approaches to the analysis of inorganic constituents in water with an emphasis on trace metals; (2) formulate methods and procedures for utilization of new field and laboratory techniques and instrumentation; (3) study specific water quality and environmental chemistry problems; (4) participate in interdisciplinary research programs; and (5) provide consultation to other projects and programs in the U.S. Geological Survey.

APPROACH: (1) Maintain a periodic review of pertinent scientific literature and communicate frequently with colleagues and consultants who are involved in similar research and development programs; (2) identify areas where improvement of existing technology can offer extended analysis capability and efficiency; (3) design and perform laboratory and field experiments that will elucidate the significance of parametric variations in water quality and environmental chemistry using statistical and factorial techniques to optimize and evaluate parametric factors; (4) prepare definitive reports and publications outlining the research findings and interpretation of data from water quality and environmental chemistry studies.

PROGRESS: (1) Research and development studies continued on the occurrence and distribution of trace metals in pristine lakes (Fremont & New Fork, Wyo., and Emerald Lake, Sequoia National Park, Calif.). Preliminary evaluation of important geochemical and atmospheric (acid rain) inputs were accomplished. Selected trace-metal budgets, mass balances, correlations, and water chemical interactions were studied. (2) 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. 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. Techniques for absolute quantitation by stable isotope dilution analyses were developed. Instrumentation modifications were investigated to improve measurement precision, stability, and sensitivity. (3) Research was continued on the use of osmosis and reverse osmosis techniques for preconcentrating heavy metals in highly dilute hydrologic systems prior to chemical analysis. Apparatus was designed and fabricated for the effective utilization of this approach for preconcentration of heavy metals in rainwater. Evaluation of the characteristics of this approach was performed. (4) Field techniques are being developed for the collection of trace metals from atmospheric precipitation to allow evaluation of the significance of input from acid rain to the hydrologic system. The use of chelating ion exchange resins to collect and concentrate trace metals was evaluated and found to be suitable for field studies. (5) Research was completed on the measurement of time-resolved ultraviolet absorption spectra from thermally vaporized organic compounds. A unique approach using multiwavelength photodiode array detection with an electrothermal graphite furnace atomizer was studied. Techniques are under development to permit the direct analysis of bed and suspended sediments from the Mississippi for polynuclear aromatic hydrocarbons. (6) Research was performed on the development of a technique suitable for measurement of field alkalinity using a microcomputer-controlled coulometric titration. (7) Research was performed and two field trips made to measure the occurrence, distribution, and fate of trace metals in the Mississippi River system. This includes the investigation of interaction of trace metals with other water chemical parameters, with emphasis on the distribution between various size fractions of suspended material (silts, colloids, etc.). Studies were performed to representatively collect and separate statistically valid and uncontaminated samples.

REPORTS PUBLISHED:

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Garbarino, J. R., and Taylor, H. E., 1987, Stable isotope dilution analysis of hydrologic samples by ICP/MS: Anal. Chem., v. 59, no. 11, p. 1568-1575.

Schroder, L. J., Brooks, M. M., Garbarino, J. R., and Willoughby, T. C., 1987, The influence of an urban environment in the chemical composition of precipitation, in Averett, R. C., McKnight, D. M., eds., Chemical quality of water and the hydrologic cycle: Lewis Publications, ch. 3, p. 39-53.

CR284 CORROSION BY WET PRECIPITATION

TITLE: Corrosion of Building Materials as Determined From Solid Weathering Products Removed by Wet Precipitation

PROJECT NUMBER: CR 83-284

LOCATION: Topical Research

PROJECT CHIEF: Reddy, Michael M.

HEADQUARTERS OFFICE: Arvada, CO

PROBLEM: Accelerated decay of stone cultural treasures and building materials is apparent in several areas of the United States. Its cause has been attributed to air pollution and acid deposition. Although this destructive process may have significant adverse effects on the economic well-being of the country, little fundamental understanding of processes involved or quantitative relations between important variables are available. Processes involved in rock-precipitation reactions are understood poorly, leading to large uncertainties in estimates of acid-precipitation impacts. Information about the influence of acid precipitation on urban runoff water quality also is lacking.

OBJECTIVE: Determine stone-dissolution processes and rates in the natural and polluted environment. To the extent feasible, separate the effects of wet deposition from the effects of dry deposition, as well as from normal weathering processes. Evaluate the influence of acid-precipitation interaction with materials on urban runoff water quality.

APPROACH: Collect and analyze rainfall leachate from selected materials at appropriate locations to obtain field measurements of acid rain damage. Washington, D.C., will be the first field site. A prototype field instrument that continuously monitors pH and conductance will be evaluated near Denver, Colo., before shipment and installation at the Washington, D.C., site. In support of the field study, use facilities and staff available at the U.S. Geological Survey Central Laboratory in Denver and establish appropriate, quality controlled, analytical methods compatible with the analysis of rainfall-leachate solutions.

PROGRESS: Completed 4 years of intermittent onsite measurement of acid rain weathering of limestone and marble at four research sites in the eastern United States. Experimental protocol was modified to assess the importance of rock wetness, rock orientation, and within-storm variation in rainfall chemistry on carbonate rock weathering. Results have been summarized in a paper published in a recent American Chemical Society Symposium Series, and are in press in Earth Surface Processes and Landforms. Carbonate stone weathering rates have been quantitatively related to acid deposition.

WRD FEDERAL RESEARCH PROJECTS.....SURFACE-WATER CHEMISTRY

REPORTS PUBLISHED:

Reddy, M. M., and Youngdahl, C. A., 1987, Acid rain and weathering damage to carbonate building stone: Results of material loss measurements: Corrosion 87 March 9-13, 1987, Moscone Center/San Francisco, Calif., Proceedings, Paper no. 415.

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See, R. B., Reddy, M. M., and Martin, R. G., 1987, Description and testing of three moisture sensors for measuring surface wetness on carbonate building stones: U.S. Geological Survey Water-Resources Investigations Report 87-4177, 16 p.

CR285 COMPREHENSIVE ORGANIC ANALYSIS OF WATER

TITLE: Comprehensive Organic Analysis of Water

PROJECT NUMBER: CR 84-285

LOCATION: Topical Research

PROJECT CHIEF: Leenheer, Jerry A.

HEADQUARTERS OFFICE: Arvada, CO

PROBLEM: A disproportionate amount of research in water chemistry has been directed towards defining trace levels of organic contaminants in water where as the structures and concentrations of natural organic solutes, which comprise most of the dissolved organic carbon (DOC), are very poorly defined. A better knowledge of the nature of natural DOC in water is essential to the advancement of many diverse sciences, such as geochemistry, aquatic biology, soil science, and even atmospheric chemistry involving carbon cycle research. The WRD is conducting significant research on the nature of humic substances in water, which comprise about one-half the DOC in water, but a comprehensive study of the entire suite of organic substances comprising DOC has been lacking.

OBJECTIVE: Conduct comprehensive organic analyses of various surface-water samples where comprehensive organic analyses is defined as "state-of-the-art" organic analyses on as many components of DOC as possible within the time and resource limitations of the project. Develop chromatographic methods for DOC separations. Define the chemical, biologic, and hydrologic processes which lead to DOC in water, as components of DOC are chemically defined.

APPROACH: Characterize algal inputs in fresh water (Island Lake, Nebr.) and saline water (Big Soda Lake, Nev.), study terrestrial vegetative contributions to DOC in the Suwannee River in southern Georgia, a subtropical environment, and in the Sagavarirtok River of Alaska, an arctic environment. Determine spatial and seasonal differences of dissolved and suspended organic carbon in the Mississippi River to determine hydrologic and biogeochemical processes on DOC in an integrating environment. Apply techniques used to study DOC to study organic contaminant transformations in ground at Cape Cod, Mass. Develop chromatographic techniques to separate DOC into its constituent compounds and determine the structure of the compounds by various spectrometric techniques.

PROGRESS: A unified system for sampling, fractionating, and dewatering suspended sediment from the Mississippi River for geochemical and contaminant analysis was developed. The system employed depth-integrated sampling, continuous-flow centrifugation, and tangental-flow ultrafiltration. Analysis of the dissolved organic solute fraction from Mississippi River samples found significant concentrations of polyethylene glycol residues throughout the

river system. These residues are degradation products of non-ionic detergents and their detection was a new discovery. A new approach for comprehensive isolation of dissolved organic solutes was developed which successively used vacuum evaporation, adsorption chromatography, and zeotrophic distillation of water from acetic acid. The significant advance in this new procedure is the separation of inorganic salts from hydrophilic organic solutes by the zeotrophic distillation procedure.

REPORTS PUBLISHED:

Leenheer, J. A., Wilson, M. A., Malcolm, R. L., 1987, Presence and potential significance of aromatic-ketone groups in aquatic humic substance: Organic Geochemistry, v. 11, no. 4, p. 273-280.

Chiou, C. T., Kile, D. E., Brinton, T. I., Malcolm, R. L., Leenheer, J. A., and MacCarthy, P., 1987, A comparison of water solubility enhancements of organic solutes by aquatic humic materials and commercial humic acids: Environmental Science and Technology, v. 21, no. 12, p. 1231-1234.

CR296 Colloid Geochemistry

TITLE: Colloid Geochemistry and Transport Research

PROJECT NUMBER: CR 86-296

LOCATION: Central Colorado

PROJECT CHIEF: Rees, Terry F.

HEADQUATER OFFICE: Denver, CO

PROBLEM: In recent years, there has been a growing realization that many organic substances, hazardous materials, heavy metals, and radioactive substances are present in natural waters not as dissolved species, but in association with dispersed microparticulates (colloids). Consequently, an additional mechanism for the transport of these substances is the movement of colloidal materials through the geosphere to the accessible environment. A limited amount is known about the nature of indigenous colloids in surface and ground waters. Similarly, knowledge is limited concerning the interactions of dissolved species with these indigenous colloids. The parameters that control the movement of colloids through different types of aquifers has never been systematically investigated. Because of these three deficiencies, it is impossible to assess the possible importance of colloid-controlled migration of hazardous substances.

OBJECTIVE: (1) Develop an improved understanding of the parameters that affect the movement of colloidal materials in surface- and ground-water systems; (2) By use of survey techniques, determine the types of indigenous colloids in a variety of surface and ground waters; (3) study size distributions and surface characteristics; (4) investigate parameters that control sorption of materials onto colloids; (5) study the parameters that control the movement of colloids in surface- and ground-water aquifers; and (6) By using these studies, assess the role of colloid-controlled migration of hazardous substances.

APPROACH: Develop procedures to collect, fractionate, and characterize colloidal materials from natural waters; make site-specific investigations on the basis of the procedures developed. Techniques currently in use include Scanning Electron Microscopy (SEM), Photon Correlation Spectroscopy (PCS, laser light scattering), Electrophoretic Light Scattering (ELS), ICP, Energy Dispersive X-ray analysis (EDAX), X-ray Diffraction, and dialysis. Techniques being evaluated for future use include Field Flow Fractionation (both sedimentation FFF and Flow FFF), Hydrodynamic Chromatography (HDC), and Capilary Flow Chromatography (CFC). These techniques should allow separating the highlypolydisperse colloidal samples into less complex mixtures more readily amenable to our other analytical techniques.

PROGRESS: Progress this past year included rebuilding the Project's laboratory, which sustained major damage as a result of a roof fire during July 1987. Project personnel participated in two successful sampling surveys of the Mississippi River from St. Louis, Mo., to Belle Chasse, La. Samples from the survey (July-August 1987) have been characterized as to particle size distribution, mineral phase composition, and colloid surface charge characteristics. Talks describing these results have been accepted for presentation at the Fine Particle Society Annual Meeting and the International Symposium on the Fate and Effects of Toxic Chemicals in Large Rivers and their Estuaries. Samples collected from St. Kevins Gulch on the Upper Arkansas River, Colo., indicate that iron removal from that acid-mine-drainage-contaminated stream is probably as a result of rapid precipitation of 50-nm iron hydroxide colloids, followed by rapid aggregation into submicron particles, then ultimately slow agglomeration of these aggregates into larger particles, which either settle, or are scavenged by cobbles in the stream bed. These results have been accepted for presentation at the upcoming American Chemical Society meeting in Toronto. Journal manuscripts are also in preparation for both the Mississippi River and the Arkansas River studies.

REPORTS PUBLISHED:

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NR065 SED.-WATER EXCHANGE OF NUT./METALS

TITLE: Sedimentary Geochemical Processes Affecting the Exchange of Nutrients and Transition Metals Between Sediment and Water in Riverine, Estuarine, and Lacustrine Environments

PROJECT NUMBER: NR 76-065

LOCATION: Topical Research

PROJECT CHIEF: Callender, Edward

HEADQUARTERS OFFICE: Reston, VA

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 only are estimated when considering biogeochemical cycling and ecological responses. Understanding geochemical processes that control nutrient and transition metal chemistry of natural waters is requisite for predicting the effects man-induced events will have upon natural geochemical cycles and for determining their utilization as a natural 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; (3) assess the influence man's activities exert on natural geochemical cycles.

APPROACH: Sample and analyze surface water, ground water, and sediment-pore water for nutrient and transition-metal content of aqueous phase 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 using 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: (1) Several gravity cores were collected from the western end of the Cheyenne River Arm of Lake Oahe, S. Dak., and processed for interstitial water. The progression of interstitial Fe, Mn, P, and As concentrations in cores taken in 1985, 1986, and 1987 indicate that molecular diffusion cannot keep pace with sediment particle accretion. Therefore, solute transport is unable to transfer contaminant constituents, such as As, from bottom sediment to the overlying water column. (2) The distribution of Cesium-137 (Cs-137) was determined in a sediment core collected in 1986 from the eastern end of the Cheyenne River Arm of Lake Oahe. The peak Cs-137 activity occurred at a depth of 130 cm. The profile of Cs-137 in the sediment core is generally

coincident with the history of deposition of radiocesium from atmospheric nuclear testing and indicates a mean sediment accumulation rate of five to seven cm/yr since the mid-1960's. Because the sedimentation rate is high, the annual cycle of Cs loading is apparent as periodic "spikes" in the profile. From the location of the spokes, the mass-sediment-accumulation rate was calculated and shown to have decreased gradually from seven to one g/cm2/yr since filling of the reservoir in 1959. These data were used to calculate the flux of arsenic and other contaminants to the Cheyenne River Arm of Lake Oahe. The distribution of Cs-137 in the core is quantitatively predicted by a model that includes direct transfers from the atmosphere plus contributions that are integrated as a result of long-term storage in the Upper Missouri River drainage basin. (3) During the fall of 1987, several sediment cores were taken in the Pueblo Reservoir (South-Central Colorado) and sampled for interstitial water and sediment solids. The vertical distribution of normalized heavy-metal data, acquired on the sediment solids, shows some pronounced peaks at depths that record sedimentary riverine inputs during the past 10 years. The core in close proximity to the mouth of the Arkansas River shows normalized Cn, Zn, Pb, Cd maxima at depths that correspond to heavy-metal "breakouts" from the Leadville, Colorado mines during 1985 and 1983. The other two cores, located farther from the riverine source, show a pronounced maxima at a depth that is indicative of contaminant inputs during 1985. (4) A 3-year water quality study in the Potomac Estuary was completed. Sediment, C and N fluxes from sediment trap deployments increased with depth of deployment due to resuspension of bottom materials. Seasonally the sediment, C and N fluxes from the traps closest to the surface (least affected by resuspension) co-varied. The lowest fluxes occurred during the summer with higher fluxes in the spring and fall. There was no direct relationship between the observed fluxes and the concentration of suspended sediment or particulate N and C in the water column. The C/N of sinking material is similar to water column particulate material except during the summer when it decreases while water column C/N ratios increase.

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NR092 URANIUM MILL TAILINGS

TITLE: Hydrogeochemical Controls on the Migration of Radionuclides from Uranium Mill Tailings

PROJECT NUMBER: NR 78-092

LOCATION: Topical Research

PROJECT CHIEF: Landa, Edward R.

HEADQUARTERS OFFICE: Reston, VA

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: Despite the fact that most of the radium-226 initially present (pre-milling) in uranium ore is typically found in the tailings solids (post-milling), there is evidence of redistribution among particle size fractions during milling. The geochemical hosts of such translocated Ra-226 and other uranium-series radionuclides have received little or no experimental attention. Studies are underway in which fresh solutions from the sulfuric acid leaching of uranium ore under simulated milling conditions have been contacted with synthetic tailings mixtures (quartz sand plus a varying, single substrate, i.e., barite, potassium and sodium feldspars, kaolinite, montmorillonite, etc.). Radionuclide contents and radon emanation coefficients of the synthetic tailings are being examined. This work is being done in collaboration with Chuck Bush, Branch of Isotope Geology, Geologic Division, Denver. X-ray diffraction analysis and radioassay of the samples is still underway. Preliminary results suggest (1) detrital and milling-generated barite may be an efficient sink for radium; and (2) radium sorbed by organic matter (sub-bituminous coal used here) has a significantly higher emanating power than seen with mineral substrates.

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NR099 GEOCHEMICAL CARBON FLUXES

TITLE: Carbon Fluxes in Hydrologic and Geologic Processes

PROJECT NUMBER: NR 79-099

LOCATION: Topical Research

PROJECT CHIEF: Sundquist, Eric T.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: Carbon fluxes are an important aspect of many hydrologic and geologic processes. For example, on a global scale, rising atmospheric carbon dioxide (CO2) concentrations and man's increasing use of fossil fuels have led to concern for the future effects of atmospheric CO2 on global climate. Anticipating the effects of atmospheric CO2 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 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. Investigate the possibility of past variations in the world's (natural) CO2 balance, and apply this information to the prediction of future global CO2 fluxes. Understand the role of fluxes of natural carbon compounds in selected local ground-water and/or surface-water contamination problems. Determine the geochemical mass balance for carbon in selected hydrologic/geologic systems.

APPROACH: Derive estimates of carbon fluxes and quantities either from direct measurements or from computer models of hydrologic and geologic processes. Determine gases using gas chromatography. Characterize organic matter using high performance liquid chromatography. Determine dissolved inorganic carbon using gas chromatographic and titration techniques. Characterize carbonate minerals by both chemical and petrographic analyses. Apply stable isotope and carbon-14 measurements to all phases, where appropriate. Incorporate these measurements into computer models based on the mass balance approach.

PROGRESS: Project activities have focused on aspects of the carbon cycle that are particularly relevant to the geochemical effects of CO2 and long-term geochemical predictions. Matrix transformations and eigenanalysis show how carbon cycle models appropriate to short timescales can be systematically related to models appropriate for long timescales. For long-term CO2 predictions (hundreds to thousands of years), modeling techniques have been

developed to accommodate carbonate dissolution and other sediment interactions. Ocean modeling suggests that if man burns all of the world's fossil fuel reserves, the average lysocline and atmospheric CO2 concentrations may remain perturbed for thousands to tens of thousands of years. The long-term predictions are subject to significant uncertainties because the present ocean/atmosphere/sediment system may not be at steady state. Based on the geologic record of oceanic carbonate dissolution, the model also suggests that geologic variations in atmospheric CO2 must have been accompanied by significant oceanic alkalinity changes. In the laboratory, gas chromatographic techniques were implemented for analyzing carbon dioxide, carbon monoxide, and methane in 1-ml soil gas samples. An automated remote soil gas sampler was readied for field testing. Also, substantial contributions were made to the development of the U.S. Geological Survey's climate program.

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NR109 TRACE METALS AND NUTRIENTS

TITLE: Geochemical Cycling of Trace Elements and Nutrients in Natural Water Systems

PROJECT NUMBER: NR 81-109

LOCATION: Topical Research

PROJECT CHIEF: Bricker, Owen P.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: Natural water systems provide a wide range of conditions in 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 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 effect of mineral-water interactions in determining the chemical composition of natural waters, with emphasis on trace elements and nutrients, to describe quantitatively the geochemical behavior of trace elements and nutrients in freshwater, estuarine, and marine environments. Assess the impacts of anthropogenic contributions on natural cycles in these systems and evaluate the hydrogeochemistry of trace elements and nutrients as a function of water resource utilization.

APPROACH: Develop geochemical mass balance studies of the flux of trace elements and nutrients in natural water systems by detailed sampling and chemical analysis of input waters and outflow waters. Identify and quantify the critical reactions that control changes in water chemistry through examination of the solids that the waters contact and react with and through laboratory studies of rock soil-water interactions. Separating solids from the solution phase requires special collection, filtration, and (or) ultra-centrifugation techniques. Examine the solid phases by chemical analysis, x-ray diffractometry, optical and electron microscopy (SEM, TEM), and special techniques for definition of the surface boundary layer. Perform chemical analysis of the aqueous phase using ion-chromatography and special potentiometric techniques. Interpret the chemical compositions of the solid and aqueous phases relative to thermodynamic and (or) kinetic behavior in the hydrochemical environment.

PROGRESS: Geochemical investigations of weathering processes in some forested eastern United States watersheds show that preliminary mineralogic investigations at the Catoctin Mountain, Md., site show the presence of a corrensite, a regular chlorite-smectite (previously unreported), in more poorly drained areas. In the Mill Run, Va., watershed, the configuration of the sediments and their geomorphology and composition determine near surface hydrologic flow paths. In the Mill Run, Va., watershed, the response of vegetation to water availability suggests a strong correlation of rainfall-runoff to near-surface sediment-soil facies changes. Dry deposition to coniferous canopies contributes up to 20 percent more sulfate than deciduous canopies. Deciduous canopies exhibit a net neutralizing effect on acid deposition inputs whereas coniferous canopies increase the acidity of the inputs. For the 1982-85 period, only 2 percent of sulfate in rain originated as sea salt. Of the remainder, 59 percent was H_2SO_4 and 39 percent originated as neutralized acids and salts of terrestrial origin. Approximately 3-9 percent of the SO_4^{2-} deposition washed from deciduous canopies and 2-7 percent washed from coniferous canopies is the result of biological cycling. The remainder of the net increase in SO_4^{2-} deposition is the result of dry deposition of gaseous and particulate SO_4^{2-}.

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NR135 SPECIATION OF METALS

TITLE: Distribution and Speciation of Metals in Sedimentary Environments

PROJECT NUMBER: NR 86-135

LOCATION: Topical Research

PROJECT CHIEF: Simon, Nancy S.

HEADQUARTERS OFFICE: Reston, VA

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 the 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 smaller 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 the 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 examining the speciation of metal complexes, and use electrochemical analysis in the determination of free and liable 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 using extraction methods or specific ion electrodes, but also with biochemical methods coupled

with liquid chromatography and electroanalytical techniques in order to determine specific information about the rexdox chemistry, chemical associations, and bioavailability of toxic metals.

PROGRESS: Statistical evaluation of data from a detailed study of sediment extraction techniques has resulted in the identification of four mechanisms for cycling chromium in Calcasieu River, La., sediments. These four mechanisms include the partitioning of chromium with the iron oxide phases, the manganese oxide phases, labile organic matter, or refractory organic matter. Chromium retained by sediment from cores collected up and downstream from petrochemical input is associated with iron oxides and organic matter subject to degradative reactions. In cores taken from two sites close to petrochemical input, manganese oxides and refractory organic matter played the largest role in sediment retention of chromium. These conclusions were based on sediment organic carbon and nitrogen data, sediment total metal concentration data, surface adsorption studies, data from extractions with pyrophosphate plus hydrogen peroxide or hydrogen peroxide plus dilute hydrochloric acid, and interstitial water metal analyses. The data suggest that the difference between chromium retention by metal oxides or organic matter could be inferred using only the sediment organic carbon data and the extraction data. Identification of metal phase association is a factor in determining metal bioavailability and mobility. A comparison was made of irradiated and non-irradiated sediment collected from a Calcasieu River site subject to petrochemical inputs. Polarographic analyses of sediment interstitial water over a period of 3 months showed progressive elevation of cadmium and lead concentrations, and increased concentrations of dissolved organic compounds which efficiently complexed the metals. The dissolved organic compounds complexed lead more efficiently than cadmium.

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WR044 SOLUTE TRANSPORT AT LOW FLOW

TITLE: Solute Transport Processes in Low-Flow Streams

PROJECT NUMBER: WR 65-044

LOCATION: Topical Research

PROJECT CHIEF: Kennedy, Vance C.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: The interaction of water and stream solids, such as abiotic material, organic detritus and biota, can affect the chemical composition of both water and solids, especially in the case of minor elements. Thus, when new solutes are added to a stream, they may behave as conservative constituents, may be adsorbed by stream solids (with or without displacement of previously adsorbed materials), may precipitate, or may combine with stream solutes to form complexes having properties quite different from the original solutes. In some respects, stream biota will behave much like abiotic solids on reacting with stream solutes, but in other aspects their behavior may be very different as, for example, in the case of nutrient uptake. A better understanding of the rate and nature of water-stream solids interaction is needed to allow quantitative predictions of the manner of transport of various dissolved constituents.

OBJECTIVE: Determine the nature and rates of the hydraulic and chemical processes involved in the interaction between introduced solutes and abiotic material plus organic detritus.

APPROACH: Inject a mixture of conservative and nonconservative solutes into streams for various time periods and intensively monitor their transport downstream. The conservative constituents serve as tracers for hydraulic transport processes independent of any reactions with stream solids, whereas the reacting nonconservative solutes (nutrients, trace and major elements) are removed from solution, permanently or temporarily, at various rates depending upon their chemistry and the nature of the stream solids (sediments and biota) with which they are interacting.

PROGRESS: Work continued on studies related to the source and isotopic composition of stream waters. Saturation of soil with water greatly enriched in deuterium and oxygen-18, followed by monitoring of the isotopic composition of the surface-soil water over about a 3-week drying period, indicates that there can be considerable interaction between soil moisture and atmospheric moisture between rainfall events. This shows, if generally true, that the isotopic composition of water reaching the ground-water table is related in a complex fashion to the soil texture, the drying interval between storms, and differences in the isotopic composition of rainfall compared to atmospheric moisture during dry periods. Such a relationship differs significantly from

the one commonly assumed, which is that the isotopic composition of groundwater is the volume-weighted average of wet precipitation in an area.

WR076 CHEMISTRY OF HYDROSOLIC METALS

TITLE: Chemistry of Hydrosolic Metals and Related Constituents of Natural Water

PROJECT NUMBER: WR 57-076

LOCATION: Nationwide

PROJECT CHIEF: Hem, John D.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Hydrosolic metals are elements that form hydroxides with low solubilities. They may form colloidal suspensions (hydrosols). Some of these elements are toxic and they may interfere in various ways with water use. Understanding the occurrence and behavior of these elements in water is complicated by effects of pH, oxidation and reduction, formation of complex ions, coprecipitation, and kinetics. Research results from this project are utilized extensively worldwide for such purposes as education and training of hydrologists and geochemists, design and operation of water wells, water treatment and waste-disposal processes, mineral prospecting, and improvement of pharmaceutical products.

OBJECTIVE: Define dilute solution chemistry of elements of interest in sufficient detail to apply findings to natural water systems; the final reports should be useful in predicting the fate of hydrosolic metals and associated substances, either in natural or polluted systems, as guides for designing optimal data collection programs and as 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 data from literature and appropriate laboratory experiments and may postulate either equilibrium closed-system or irreversible open-system conditions. Test models in chemical laboratory experiments and apply to field data to determine applicability. Modify models, as necessary, to allow for kinetic and biochemical factors.

PROGRESS: Recent laboratory work has shown that interactions among aluminum monomeric hydroxy cations to form polymeric cationic species can occur near pH 5.0 and, if the supersaturation with respect to microcrystalline gibbsite is kept low enough, the polymeric ions do not reach diameters much greater than about 20 angstrom units. This size is near the lower limit for solid-state behavior of aluminum hydroxide particles. The growth of polymeric species is inhibited at temperatures below 25 °C, both by slower kinetics and the increased solubility of gibbsite observed at lower temperatures. The polymeric ions have a strong positive charge and may be important in the environmental impacts of acid precipitation and mine drainage. A compilation of the best available chemical equilibrium data for aqueous monomeric aluminum

species has been prepared. A review of literature and results of current research is being used to help understand the role of aluminum hydroxide crystal structure in governing the surface chemical properties of the microcrystalline materials. Small concentrations of dissolved oxalate in solution can prevent Mn_3O_4 (hausmannite) from altering to MnOOH (manganite) during aging as long as 1 year. The alteration can be nearly complete in about 2 months in the absence of organic solutes. The effect appears to be related to attachment of oxalate ions to potentially active surface sites. A mechanistic, nonequilibrium model has been developed to explain smectite clay formation and provide thermodynamic stability estimates for the compositionally heterogeneous smectite clay minerals.

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SURFACE-WATER HYDROLOGY

CR228 RAINFALL-RUNOFF MODELING

TITLE: Precipitation-Runoff Modeling of Watershed System

PROJECT NUMBER: CR 77-228

LOCATION: Topical Research

PROJECT CHIEF: Leavesley, George H.

HEADQUARTERS OFFICE: Lakewood, CO

PROBLEM: (1) Energy-resource development, urbanization, forestry practices, and other land-use changes can have a significant effect on watershed hydrology. Computer modeling techniques that simulate the physical processes of the hydrologic cycle, using measurable watershed and climatic characteristics, must be developed to adequately predict and assess the effects of current or proposed land-use changes on watershed hydrology. (2) Eruptions of Mount St. Helens deposited large quantities of volcanic ash in major tributary basins to the Columbia River. An understanding of the infiltration and erosion processes taking place on the ash deposits must be obtained to estimate the effects of this ash on runoff and erosion rates.

OBJECTIVE: (1) Test, verify, and enhance the distributed parameter Precipitation-Runoff Modeling System (PRMS) which was developed by this project to predict runoff, sediment yields, and water-balance relations for normal and extreme rainfall and snowmelt on land used in a variety of ways; develop a statistical theory of errors for the PRMS; develop model parameter estimates to relate parameters to measurable watershed and climatic characteristics. (2) Determine the infiltration and erosion characteristics of volcanic ash on selected study plots; evaluate the processes influencing these characteristics; extrapolate the plot-study results to larger basin areas using the PRMS to estimate the impacts of the ash deposits on watershed hydrology.

APPROACH: (1) Examine data from past and current small-watershed studies of the U.S. Geological Survey (for example, small-stream, coal, and oil-shale programs), other Federal agencies, and universities for the physiographic and climatic regions of the United States; evaluate the PRMS components with regard to the significant hydrologic processes in each region and enhance through modification and additional research where required; assess the sources of model error and the transfer of these errors to the model output; evaluate rainfall simulator for infiltration and erosion parameter estimation. (2) Install small plots to monitor runoff and erosion from rain and snowmelt; determine infiltration and erosion rates from these data and relate to hydrologic and ash characteristics.

PROGRESS: Work continued on defining the sources and magnitudes of precipitation input errors and their effect on snowmelt-runoff simulation errors. Spatial and temporal variability in monthly and seasonal precipitation amounts were identified for selected basins in the western United States. Procedures to account for this variability in snowmelt-runoff simulations using point, airborne, and satellite measures of snowpack water equivalent and areal extent are being investigated. Procedures to automate the characterization of a watershed into hydrologic response units (HRU) using digital terrain data, satellite imagery, basin-characteristic data bases, and GIS technology continued. Watersheds in Montana and California are being used in the initial development and testing. An interactive graphical user interface was developed for the PRMS. The interface uses a GIS-developed characterization of a watershed for user interaction. Expert systems technology is used to assist users in parameter value selection. Simulation results for streamflow and all model state variables can be user selected for display by individual HRU's or for the entire basin. A study in cooperation with the World Meteorological Organization was initiated to compare the accuracy of selected precipitation gages and wind shields in the measurement of solid precipitation. The study site was located at Rabbit Ears Pass in Colorado. Regional trends in log Pearson III flood-frequency statistics were investigated using rainfall-runoff modeling. Calibrated rainfall-runoff model parameters for 200 small basins and maps depicting the influence of climate on floods were used to develop average values for the mean, standard deviation, and coefficient of skew at 100 km grid intervals for an area of about 4.7 x 10**6 sq km east of the 105th meridian. Strong regional trends are evident in all derived statistics and suggest that point estimates may have utility in improving T-year flood estimates at short record sites.

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CR279 ERRORS ANALYSIS

TITLE: Statistical Analysis of Errors in Hydrologic Models

PROJECT NUMBER: CR 83-279

LOCATION: Topical Research

PROJECT CHIEF: Troutman, Brent M.

HEADQUARTERS OFFICE: Lakewood, CO

PROBLEM: Application of hydrologic models without an analysis of the errors can be misleading. Proper interpretation of model output through analysis of errors can eliminate economic consequences of over- and under-design resulting from model-related errors.

OBJECTIVE: (1) Develop unified approach to analyzing and partitioning errors in hydrologic modeling; (2) develop improvements to existing practices; and, (3) develop new approaches to managing error levels within the constraints of reduced budgets.

APPROACH: Use concepts of linear and nonlinear regression and optimal interpolation and prediction to estimate the individual contributions of space, time, and model error in hydrologic modeling.

PROGRESS: The value of instantaneous unit hydrograph (IUH) theory in defining the runoff response characteristics of a drainage basin was examined, and new expressions for the IUH of a basin were derived. These expressions are functions of only a few quantities, some of which are readily obtainable from a map of the basin: magnitude, order, diameter, Horton's ratios, and link-length properties. Derivations of some of these expressions utilized results in geomorphology for the so-called random topology model and results in probabilistic branching theory. Extensions have been made to nonlinear channel routing schemes using simulation techniques, and the connection of basin-scale relations to relations obtained via traditional regionalization methods has been explored. Also, a new spatial random network model based on elementary postulates has been developed and tested. Statistics for networks generated by this new model compare favorably to values for naturally occurring networks.

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Karlinger, M. R., Guertin, D. P., and Troutman, B. M., 1988 Regression methods for topological hydrograph input: Journal of Water Resources Planning and Management: American Society of Civil Engineers, v. 114, no. 4, p. 446-456.

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CR301 ORGANIC SUBSTANCES IN STREAMS

TITLE: Transport and Degradation of Organic Substances in Streams

PROJECT NUMBER: CR 77-301

LOCATION: Topical Research

PROJECT CHIEF: Rathbun, Ronald E.

HEADQUARTERS OFFICE: Lakewood, CO

PROBLEM: Organic substances in streams affect the water 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 using these coefficients must then be developed for predicting the fate of organic substances in streams and their effect on water quality.

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

APPROACH: (1) Controlled laboratory studies of the volatilization and sediment sorption of specific organic compounds, both as single components and as mixtures; (2) controlled field studies of the testing, adapting, and developing of transport and fate models for organic substances in streams; and (4) application of the models to field problems.

PROGRESS: An outdoor model stream experiment indicated that the fates of acetone and t-butyl alcohol were determined primarily by the process of volatilization. Glucose was microbially degraded. Small losses of rhodamine-WT dye were apparently the result of photochemical and sorption processes. Failure of the acetone to degrade microbially was contrary to expectations based on laboratory studies. This result indicates that prediction of the fate of organic compounds in streams on the basis of process studies in the laboratory may be subject to error. An analysis showed that the liquid-film and gas-film reference substance parameters for predicting stream volatilization coefficients could be estimated from the solute molecular weight and molal volume with mean absolute errors of less than 8 percent.

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Rathbun, R. E., 1988, Discussion of "Wind function for a sheltered stream": American Society of Civil Engineers Journal of Environmental Engineering, v. 114, no. 1, p. 229-231.

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Tai, D. Y., and Rathbun, R. E., 1988, Photolysis of rhodamine-WT dye: Chemosphere, v. 17, no. 3, p. 559-573.

NR019 NUMERICAL SIMULATION

TITLE: Numerical Simulation of Hydrodynamic Processes in Rivers, Estuaries, and Embayments

PROJECT NUMBER: NR 69-019

LOCATION: Topical Research

PROJECT CHIEF: Baltzer, Robert A.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: Technical solutions to the problem of investigating and managing waste movement and disposal in regulated rivers, estuaries, and embayments require qualitative and quantitative assessment 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 both 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) Thoroughly explore the hydrodynamics of one-, two-, and three-space dimensional transient flows in waterways and waterbodies (including the transport and interaction of constituents); (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 regimen 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: Conducted a partial analysis of the nonhomogeneous terms in the unsteady flow equation set used in BRANCH, the one-dimensional, network flow model and subsequently reported these preliminary findings at the National Conference, American Society of Civil Engineers (ASCE). Studied various approaches to treating overbank storage in one-dimensional flow models, particularly with respect to implicit method of characteristics (IMOC) numerical technique based on flow and cross section (Q,A) as the dependent variables. Formulated a general purpose means for handling internal boundary conditions (all eight hydrodynamic possibilities) for incorporation into a one-dimensional, flow model. Revised parts of the one- and two-dimensional model support systems, Geographic Data Analysis System (GDAS) and Time Dependent Data System (TDDS), so that they may be operated interactively on super microcomputers and computing work stations. Devoted considerable time and effort to restoring parts of the two-dimensional, flow/transport modeling system, SIMSYS2D, to full operation on the IBM/Amdahl mainframe computing system and to adapting it to operate on the Prime minicomputer system. Used the geographic information system (GIS) ARC/Info to manipulate and process digital line graph (DLG) data and digital land-use/land-cover data provided by National Mapping Division to develop a new technique for implementing two- and three-dimensional models. Provided assistance, project consultation, and training to District Offices planning or already using one- and two-dimensional modeling techniques devised by this project or by the associated research group.

Lai, C., Schaffranek, R. W., and Baltzer, R. A., 1987, Nonhomogeneous terms in the unsteady flow equations: Modeling aspects: 1987 National Conference on Hydraulic Engineering, American Society of Civil Engineers, Williamsburg, Va., August 3-7, Proceedings, p. 351-358.

NR096 COMPUTATIONAL HYDRAULICS

TITLE: Computational Hydraulics for Surface Water Problems

PROJECT NUMBER: NR 79-096

LOCATION: Topical Research

PROJECT CHIEF: Lai, Vincent C.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: Because of rapid change in computer capability and computing milieu and involvement of Water Resources Division in computer modeling of various practical water problems, many research hydrologists find little time for carefully appraising up-to-date numerical tools and modeling techniques. Use of inadequate computational methods and numerical analysis, improper handling of parameters and data for numerical modeling, and application of questionable or outdated modeling techniques, all lead to serious simulation errors or total information losses. Relatively little work has been done for numerical analysis; moreover, the previous work largely has been limited to simple, linear, and idealized flow conditions far from real-world problems. Also, relatively few people are aware that present-day computer modeling requires much broader knowledge and techniques than numerical analysis.

OBJECTIVE: (1) Investigate, compare, or appraise various numerical approaches, methods, schemes, or modeling techniques for hydraulic or hydrodynamic simulation, explore or test newly introduced numerical methods for their adequacy and applicability in hydrologic projects, and devise or develop new numerical modeling approaches for simulating surface-water problems; and (2) conduct studies on numerical stability, convergence, accuracy, efficiency, parameter identification, and sensitivity analyses associated with nonlinear schemes or models in computational hydraulics and water resources problems that are more complex but physically more realistic than linear schemes and models.

APPROACH: (1) Review existing and newly introduced numerical approaches, methods, schemes, and modeling techniques. Investigate, for given flow problems, the effect that changes in numerical schemes and modeling methods have on simulation results. Compare relative merits of different methods and techniques from various viewpoints; and (2) review physical concepts of nonlinear effects in various flow problems, rapidly-varied unsteady flows in particular; study the roles of nonlinear and higher-order terms in partial differential equations, and investigate the effects of these terms in different numerical schemes.

PROGRESS: An intensive investigation is being made on nonhomogeneous terms in the partial differential equations describing unsteady open-channel flows. While a variety of nonhomogeneous terms makes the numerical model more versatile and adaptable to varied flow conditions, these terms also strongly influence computational efforts, accuracy, stability and other numerical properties; qualitative and quantitative study of these terms will lead to sound guidelines for model developers and users. Two new schemes were developed to model unsteady fixed-bed open-channel flow by the multimode method of characteristics: (1) Multimode scheme of the first kind is an innovative numerical scheme which combines the implicit, temporal reachback, spatial reachback and classical schemes into one; it is valid for all range of the Courant number, and does more work than the combined capacity of the individual schemes involved; (2) multimode scheme of the second kind is another new numerical scheme which combines the spatial reachout, temporal reachout, spatial reachback, temporal reachback and classical schemes into one; although it requires a long reach to be advantageous, it requires much less programming efforts and computer time than the preceding scheme and has the same capacity and covers the same flow range. Work on modeling unsteady movable-bed open-channel (alluvial-channel) flow by the multimode method of characteristics continues; both the numerical method and the application problems addressed are new and the unsteady sediment flow simulation has been extended to a tidal reach having flow reversal, lateral sediment inflows, nonprismatic channel and other complexities. The numerical analysis on the multimode method of characteristics has been extended from stability analysis to accuracy analysis, and a number of "amplitude and phase portraits" have been obtained. The use of the multimode method of characteristics in unsteady, nonhomogeneous density flow, stratified flow, 2-D flows, and salinity intrusion is being explored.

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Lai, C., in press, Comprehensive method-of-characteristics models for flow simulation: Journal of Hydraulic Engineering, American Society of Civil Engineers, v. 114, no. 9.

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NR104 MODELING OF HYDRODYNAMIC SYSTEMS

TITLE: Simulation Modeling of Hydrodynamic Systems

PROJECT NUMBER: NR 80-104

LOCATION: Topical Research

PROJECT CHIEF: Schaffranek, Raymond W.

HEADQUARTERS OFFICE: Reston, VA

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 via mathematical/numerical simulation models. To accurately simulate both the temporal and spatial variations of the 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, non-uniform geometric configurations, and other human-made 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 waterbodies; (2) evaluate and (or) develop methods to describe the transport of solutes in such waterbodies utilizing 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, use to provide the required boundary-condition information with which to effect the numerical solution.

PROGRESS: Formulated and incorporated treatment of overbank storage conditions, added automatic calibration capability, and effected further enhancements and extensions in a network flow/transport model that can be used on a microcomputer. Conducted partial analyses of the nonhomogeneous terms of the unsteady flow equations and reported preliminary findings at the American Society of Civil Engineers (ASCE) National Conference. Developed microcomputer version of various components of the time-dependent data support system for hydrodynamic transport models. Provided consultation and assistance to District Offices contemplating, or actively conducting, model investigations using methods and techniques developed within the research project. Documented Potomac Estuary Study hydrodynamic transport model development effort for inclusion in a U.S. Geological Survey Water-Supply Paper.

REPORTS PUBLISHED:

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NR125 REGRESSION AND DATA-NETWORK DESIGN

TITLE: Hydrologic Regression and Data-Network Design in Coal Mining Regions

PROJECT NUMBER: NR 82-125

LOCATION: Topical Research

PROJECT CHIEF: Tasker, Gary D.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: There is a need to develop methods by which the Water Resources Division's hydrologic-data-collection activities in coal-mining regions 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 in coal-mining regions.

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

PROGRESS: A comparison of two network design methods was made for the World Meteorological Organization (WMO). The two methods, Network Analysis for Regional Information (NARI) and Generalized Least Squares Network Analysis (GLSNA) were compared using stochastic simulation in which real data from the central part of the United States were randomly resampled. Preliminary results favor the GLSNA method. A study of the effects of climate change on the water supply of the Delaware River basin was begun. This will be a 2 year effort to model the monthly flows in the basin, which includes the New York City Reservoir System, in order to evaluate changes in risks of water shortages associated with changes in rainfall and temperature predicted by Global Circulation Models (GCM). The operational Generalized Least Squares (GLS) regression method along with the GLSNA network design method have been fully implemented into an interactive computer program for regional flood frequency analysis. A method for predicting loads for 10 water quality constituents was developed and tested using GLS regression. The method is expected to be widely used for estimating non-point loads for urban watersheds.

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NR133 REGIONAL HYDROLOGIC PROCESSES

TITLE: Stochastic Structure of Regional Hydrologic Processes

PROJECT NUMBER: NR 84-133

LOCATION: Topical Research

PROJECT CHIEF: Landwehr, Jurate M.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: The regional nature of hydrologic processes is generally defined in terms of shared meteorologic and basin charactersitics. 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. Longer 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 studied.

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

APPROACH: Use both the statistical theory of extremes and time series analysis to analyze the distribution of flows as expresssed 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 databases that will be developed for this project. Use other surrogate hydrologic records, such as dendrochronologic records, ice core records, etc., as needed and available.

PROGRESS: Work has begun on the development of a U.S. Geological Survey Hydroclimatic Data Network: all District offices have responded and the information is being compiled. A draft copy of a movie depicting annual discharge patterns in the U.S. since 1921 has been completed, and visually represents spatial and temporal hydroclimatic patterns. Analysis has begun on global discharge records for comparison of large scale hydrologic variations.

REPORTS PUBLISHED:

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Slack, J. R., and Landwehr, J. M., 1988, Initial formation of the U.S. Geological Survey Hydroclimatic Data Network: Proceedings of the Fifth Workshop on Climatic Variability of the Eastern North Pacific and Western North America, March 20-24, 1988, Pacific Grove, Calif., p. 56.

NR143 LEOPOLD OPERATIONS

TITLE: Research Vessel Leopold Operations in Potomac River, Chesapeake Bay, and Adjacent Coastal Waters

PROJECT NUMBER: NR 88-143

LOCATION: Topical Research

PROJECT CHIEF: Grove, David B.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: A stable moving platform is needed to accommodate scientists 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, crew and captain.

PROGRESS: Provided research vessel support for several projects whose research is the tidal Potomac River and Estuary, Chesapeake Bay and adjoining coastal waters. Projects using vessel included ones related to microbiology, geochemistry, chemistry, and benthic ecology hydrodynamics.

WR064 ICE MODELING AND REMOTE SENSING

TITLE: Polar Ice Remote Sensing

PROJECT NUMBER: WR70-064

LOCATION: Arctic Ocean

PROJECT CHIEF: Campbell, W. J.

HEADQUARTERS OFFICE: Tacoma, WA.

PROBLEM: Variations of the major components of the cryosphere--snow packs, sea ice, and ice sheets--and their role in the hydrologic cycle, both worldwide and regional, essentially are unknown. Two major technological advances which have occurred in the last decade now make it possible to attack this problem: (1) Active and passive microwave sensors in space permit observation of many key cryospheric parameters on global scales at time intervals as short as 2 days; (2) Coupled atmosphere-sea ice-ocean numerical models make it possible to use these space microwave data to perform cause and effect simulation of cryospheric variations.

OBJECTIVE: (1) Numerically model the Arctic and Antarctic sea-ice covers and ice sheets for a variety of different rheological assumptions; (2) acquire data to test the numerical models of the Arctic and Antarctic ice sheets and ice packs by directly participationg in remote-sensing and surface-truth experiments and from remote-sensing polar-orbiting satellites; (3) investigate the dynamics and thermodynamics of the upper ocean and their relation to the ice thickness, to obtain results to be applied to the sea-ice cover models; (4) construct multi-dimensional time-dependent models of glacier flow and ice-sheet flow and to test them with observations of glaciers; and (5) investigate the use of satellite passive microwave data for snow water equivalent mapping.

APPROACH: (1) Initiate a Sea Ice Sheet Program with the U.S. National Aeronautics and Space Administration (NASA) involving 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 snow packs, sea ice, and ice sheets; and (5) develop models for sea ice, glacier, and ice sheet dynamics.

PROGRESS: Published results (6 papers) from Marginal Ice Zone Experiment (MIZEX) in a special edition of the Journal of Geophysical Research on Marginal Ice Zone studies as well as in a special section of Science. Published joint NASA-Survey treatise on the Nimbus-5 Electronically Scanning Microwave (ESMR) Arctic 4-year data set. Met with Professor Xie of the Peoples Republic of China and formulated a plan for joint snow and ice research. A scientist from France visited for 6 months and a scientist from Norway spent 3 months; they carried out cooperative research on microwave remote sensing of snow. The joint Survey-NASA Colorado Basin snow-microwave study was continued. Construction of an Antarctic icesheet radar system was finished and tested in preparation for a Survey- National Science Foundation Antarctic field program. The bedrock topography of Greenland was successfully mapped as part of the site selection for a new ice core. The Survey, NASA, and the Environmental Research Institute of Michigan field tested components of the snow-ice dielectric system (SIDS). A snow microwave workshop, an international workshop on Seasonal Ice Zone Experiment (SIZEX) studies, and a U.S. Geological Survey glacier modeling workshop were organized, hosted, and chaired. Participated in Norwegian Continental Shelf Experiment (NORCSEX).

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WR140 HYDRODYNAMICS OF TIDAL ESTUARIES

TITLE: Hydrodynamics and Mathematical Modeling of Circulation and Transport Phenomena in Tidal Estuaries

PROJECT NUMBER: WR 76-140

LOCATION: San Francisco Bay area

PROJECT CHIEF: Cheng, Ralph T.

HEADQUARTERS OFFICE: Menlo Park, CA

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

APPROACH: Include both 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. After the models are calibrated and verified, use numerical models as research tools for investigations of short and long-term transport phenomena.

PROGRESS: Emphasis of the modeling research was placed on a systems approach to solutions of the problem. A bathymetry data base, a field data archives system, along with several models have been developed and integrated

into a modeling system. At present, a tidal circulation model of any sub-embayment of San Francisco Bay can be implemented easily as needed. The models will be capable of simulation and prediction of tides and tidal currents with an estimated accuracy of 85 to 90 percent. Further research will be focused on improving the accuracy of the models so that meaningful simulations for long-term transport processes can be derived based upon the results of these hydrodynamic models. The basin bathymetry of San Francisco Bay is extremely complicated; several numerical models have been developed and implemented to satisfy the needs of a varied nature of the modeling tasks. These models include: (1) a mixed mode Eulerian-Lagrangian method for unsteady flows in the Delta, (2) a laterally averaged model for northern San Francisco Bay, and (3) a spectral model for the entire San Francisco Bay. Several reports are in preparation, including the documentation of models, user's manual and research results. Most of the reports will be published in FY 1988 or FY 1989. Although the interagency modeling group for San Francisco Bay, formed in 1985, was reorganized, collaboration on modeling research among participating agencies continued; this project provided technical advice to the overall modeling research and technical advice and support to the field data collection program.

REPORTS PUBLISHED:

Cheng, R. T., 1988, Eulerian and Lagrangian modeling of estuarine hydrodynamics, in Kjerfve, B., ed., Hydrodynamics of Estuaries, v. 1: CRC Press, Chapter 9, p. 149-159.

Cheng, R. T., 1987, Is Stokes' drift controlling long-term transport?, Proceedings of Workshop on Hydrodynamics of San Francisco Bay/Delta, p. 54-57.

Burau, J. R. and Cheng, R. T., 1987, Predicting tidal currents in San Francisco Bay using a Spectral model, Proceedings of Workshop on Hydrodynamics of San Francisco Bay/Delta, p. 81-84.

Gartner, J. W. and Cheng, R. T., 1987, Propagation of tides in South, Central, and San Pablo bays, Proceedings of Workshop on Hydrodynamics of San Francisco Bay/Delta, p. 34-37.

WR156 POLARIS OPERATIONS

TITLE: Research Vessel Polaris Operations in San Francisco Bay and Adjacent Coastal Ocean

PROJECT NUMBER: WR 77-156

LOCATION: Topical Research

PROJECT CHIEF: Conomos, T. John

HEADQUARTERS OFFICE: Menlo Park, CA

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 crew.

PROGRESS: Provided research vessel support for several projects whose research is in San Francisco Bay and other Pacific Coast estuarine systems.

WR175 ALASKA GLACIOLOGY

TITLE: Alaska Glaciology

PROJECT NUMBER: WR 66-175

LOCATION: Alaska Statewide

PROJECT CHIEF: Mayo, Lawrence R.

HEADQUARTERS OFFICE: Fairbanks, AK

PROBLEM: Glaciers produce 25 to 50 percent of the river runoff and the highest flood runoff in Alaska. Glaciers comprise the largest freshwater storage system in Alaska and also in the world, and change rapidly with small changes in climate. The basic stability and instability mechanisms of glacier flow and glacier hydrology are poorly understood or, as yet, undiscovered. Verification of hypotheses is slow because continuous high quality data of climate, glacier-mass exchange, glacier-flow behavior, and glacier hydrology are limited to short time periods at a few glaciers in Alaska. As a result, a proven conceptualization of the processes is inadequate, and predictive models are either nonexistent or generally inadequate to assess even simple problems such as predicting the effect of a 1 degree Celsius warming of the climate.

OBJECTIVE: (1) Measure and analyze mountain climate and glacier processes to verify or discover cause-and-effect relationships and determine response characteristics of glacier-related hydrologic systems; (2) study regimes of glaciers that present specific types of hazards or benefits; (3) understand the complete cycle of glacier behavior, advise of specific hazards, assess glaciers as a resource, and develop and use methods of prediction of glacier behavior; and (4) assess the importance of Alaskan glaciers to interpretation of climate.

APPROACH: Maintain instrumentation at several glaciers of different climate areas to obtain continuous measurements of high-altitude climate, snow and ice balance, and glacier flow. Analyze baseline data; develop new techniques in glaciology; conduct research studies at hazardous surging glaciers, ice-dammed lakes, calving glaciers, and other glaciers as needed, to obtain new knowledge of these hazards; and develop new scientific knowledge of glaciological principles and processes. Develop numerical models relating climate to glacier balance, glacier flow, and glacier runoff.

PROGRESS: Preliminary analyses of fathometer and ice radar data from Hubbard Glacier, Alaska, indicate that it is advancing as the result of progressive glacial erosion and fiord deposition of a submarine moraine deposit located near the glacier terminus. These processes likely will result in continued glacier advance and a reclosure of Russell Fiord in a few years. The October 8, 1986, outburst from Russell Fiord, following closure

of the body of water by Hubbard Glacier in May 1986, was probably the largest water outburst of any kind to take place during historic times. The peak discharge rate was about 105,000 cubic meters per second averaged over one hour, and a total of 5.3 cubic kilometers of water was released during the 30 hour-long event. During 1987, unusual amounts of precipitation fell on south central Alaska. At Yakutat, 6.38 meters of rain and snow fell during 1987. The average precipitation for Seattle, for comparison, is about 1.0 meter per year. Glaciers in southern Alaska are responding to this high precipitation by growing, because much of the precipitation in the glacier-clad mountains is snow, even during the summer.

REPORTS PUBLISHED:

Mayo, L. R., in press, Advance of Hubbard Glacier and closure of Russell Ford, Alaska--Environmental effects and hazards in the Yakutat area in Galloway, J. P. and Hamilton, T. D., eds., Geologic studies in Alaska by the U.S. Geological Survey during 1987: U.S. Geological Survey Circular 1016.

WR183 ANALYSIS AND MODELING OF TRANSPORT PROC

TITLE: Analysis and Modeling of Conservative and Nonconservative Transport Processes

PROJECT NUMBER: WR 83-183

LOCATION: Central California, Southeastern Alaska

PROJECT CHIEF: Walters, Roy A.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: The biological and chemical characteristics of aquatic environments depend upon a generally complicated balance of physical, chemical, and biological processes. An understanding of transport processes, including both advection and mixing is basic to describing these characteristics 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 and the interaction between man's activities and the natural processes is uncertain.

OBJECTIVE: (1) Understand the physical processes responsible for the transport of conservative and nonconservative solutes of biological and chemical importance; and (2) develop conceptual statistical, and numerical models of these processes through the use of time series analysis and other methods.

APPROACH: Use both data analysis and numerical models as diagnostic tools. The data analysis includes, but is not limited to, the application of digital filters to examine daily the seasonal time-scale phenomena, spectral analysis, empirical orthogonal function analysis, and multiple regressions. The numerical models include both box and finite element models in one, two, and three dimensions.

PROGRESS: Analysis of current meter, sea level, and salinity data has led to an improved understanding of circulation and mixing in San Francisco Bay. Development of finite-element tidal and residual circulation models has allowed a quantitative analysis of circulation in San Francisco Bay, and the North Sea and English Channel. Interdisciplinary studies include an oceanographic investigation of subglacial outflow of fresh water into an unusual Alaskan fjord, time-series analysis of glacier speed variations due to sea level changes at the terminus, and an investigation of the variations in glacial mass balance in relation to large-scale climatic influences.

REPORTS PUBLISHED:

Walters, R. A., 1987, A model for tides and currents in the English Channel and southern North Sea: Advances in Water Resources, v. 10, p. 138-148.

Walters, R. A., and Dunlap, W. W., 1987, Analysis of time series of glacier speed: Columbia Glacier, Alaska: Journal of Geophysical Research, v. 92(B9), p. 8969-8975.

Walters, R. A., Josberger, E. G., and Driedger, C. L., 1988, Columbia Bay, Alaska: An "upside-down" estuary: Estuarine, Coastal and Shelf Science, v. 26.

WR187 FLOW AND GEOCHEMICAL INTERACTIONS

TITLE: Coupled Transport and Geochemical Processes Determining the Fate of Chemicals in Surface Waters

PROJECT NUMBER: WR 84-187

LOCATION: Topical Research

PROJECT CHIEF: Bencala, Kenneth E.

HEADQUARTERS OFFICE: Menlo Park, CA

PROBLEM: Chemicals introduced into a stream react in response to a variety of homogeneous and heterogeneous geochemical processes. Transport characteristics of these chemicals are affected by such processes and biota may be influenced. The interactions are both physical and chemical, and occur over a wide range of time and distance scales. Although individual processes may be well understood, the coupling of the processes is not. The ability to quantify the interactions is very limited. The combined transport and geochemical processes determine the fate of chemicals naturally present in the environment as well as those introduced by anthropogenic activities.

OBJECTIVE: (1) Improve knowledge of the mechanisms of solute transport in streams; (2) develop experimental field techniques and mechanistic formulations of reactive transport for solute-solid interaction; (3) develop solute-transport models which are consistent with the availability of parametric field information and field verification data to aid in our ability to interpret and quantify processes; and (4) as the need arises, develop techniques for parameter estimation and model verification.

APPROACH: Analyze data from detailed dynamic field experiments. Work in pristine and acid-impacted streams. Concentrate on: (1) Development of experimental field techniques; (2) development of conservative simulations to quantify hydrologic processes, and (3) development of reactive simulation codes to quantify specific geochemical interactions. Work in the mountain-watershed environment. Study headwater streams because they form the 'boundary conditions' for larger stream systems and thus collectively influence regional water quality. Cooperate with other scientists interested in quantifying transport interactions in stream ecosystems.

PROGRESS: In the naturally acidic Snake River (Summit County, Colorado), comparisons of lithium transport with cholride and sulfate transport substantiated the use of lithium as a nonreactive tracer. The further analysis of physical transport characteristics indicated that solute sources distributed along the stream are a source of significant in-stream chemical variation. In pristine Little Lost Man Creek (Orick, California) analysis of chloride and nitrate transport experiments has shown physical storage of nitrate to be a significant factor, along with biotic processes, in nutrient retention.

Within the complete channel cross-section, the capacity of the hyporheic zone for transient solute storage and as a biological habitat varies over short distances of stream reach. In the acid mine drainage St. Kevin Gulch (Leadville, Colorado--Upper Arkansas River Toxic Substances Hydrology Site), photoreduction of ferric iron results in a well-defined increase in dissolved ferrous during day-light hours. An in-stream injection of lithium tracer allowed estimation of in-stream production.

REPORTS PUBLISHED:

Bencala, K. E., McKnight, D. M., and Zellweger, G. W., 1987, Evaluation of natural tracers in an acidic and metal-rich stream: Water Resources Research, v. 23, no. 5, p. 827-836.

Bencala, K. E., and McKnight, D. M., 1987, Identifying in-stream variability: Sampling iron in an acidic stream, in Averett, R. C., and McKnight, D. M, eds., Chemical Quality of Water and the Hydrologic Cycle: Chelsea, Mich., Lewis, p. 255-269.

McKnight, D. M., Kimball, B. A., and Bencala, K. E., in press, Iron photoreduction and oxidation in an acidic mountain stream: SCIENCE, v. 240, no. 4852, p. 637-640.

Peterson, D. H., Perry, M. J., Bencala, K. E., and Talbot, M. C., 1987, Phytoplankton productivity in relation to light intensity: A simple equation: Estuarine, Coastal and Shelf Science, v. 24, p. 813-832.

Triska, F. J., Pringle, C. M., Goldsborough, L., Robinson, G. G. C., Bencala, K. E., Zellweger, G. W., Bjork-Ramberg, S., in press, Chapter 5 iii, In Situ Manipulations, in Wetzel, R., ed.: Manual of Periphyton Methods, The Hague, Junk Publishers, p. 48.

Bencala, K. E., McKnight, D. M., Zellweger, G. W. and Goad, J., 1986, The stability of Rhodamine WT dye in trial studies of solute transport in an acidic and metal-rich stream: U.S. Geological Survey Water-Supply Paper 2310, p. 87-95.

Bencala, K. E., McKnight, D. M., Zellweger, G. W., and Kimball, B. A., Monitoring acidic streams for transport studies, in Mallard, G. E., ed., Proceedings Technical Meeting, Surface-Water Contamination, U.S. Geological Survey Toxic Substances Hydrology Program, Denver, Colo., February 2-4, 1987: U.S. Geological Survey Open-File Report 87-764.

Zellweger, G. W., Bencala, K. E., McKnight, D. M., Hirsch, R. M., and Kimball, B. A., Practical aspects of tracer experiments in acidic, metal enriched streams, in Mallard, G. E., ed., Proceedings Technical Meeting, Surface-Water Contamination, U.S. Geological Survey Toxic Substances Hydrology Program, Denver, Colo., Feb. 2-4, 1987: U.S. Geological Survey Open-File Report 87-764.

Kimball, B. A., Bencala, K. E., McKnight, D. M., and Maura, W. S., Geochemistry of dissolved metals in St. Kevin Gulch, an acidic mountain stream near Leadville, Colorado, in Mallard, G. E., ed., Proceedings Technical Meeting, Surface-Water Contamination, U.S. Geological Survey Toxic Substances Hydrology Program, Denver, Colo., Feb. 2-4, 1987: U.S. Geological Survey Open-File Report 87-764.

McKnight, D. M., Kimball, B. A., Bencala, K. E., Photoreduction of hydrous iron oxides in acidic mountain streams, in Mallard, G. E., ed., Proceedings Technical Meeting, Surface-Water Contamination, U.S. Geological Survey Toxic Substances Hydrology Program, Denver, Colo., Feb. 2-4, 1987: U.S. Geological Survey Open-File Report 87-764.

WR194 FLUVIAL MECHANICS

TITLE: Fluvial Processes and River Mechanics

PROJECT NUMBER: WR 83-194

LOCATION: Topical Research

PROJECT CHIEF: Chen, Cheng-lung

HEADQUARTERS OFFICE: Menlo Park, CA

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 incompletness of existing empirical formulas (or models) representing the relationships between various processes and responses.

OBJECTIVE: Seek a full understanding of varioius 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 which 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, etc. 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 continued both in theoretical and experimental aspects. Major tasks in progress are: (1) the development of a generally applicable macroscopic (continuum-mechanics-based) model for describing the rheological properties of various sediment-water mixtures; (2) the formulation of a general hydraulics-based routing model for simulating an unsteady debris flow at various stages of growth and subsidence, namely from its initiation to termination, as well as two transitions from landslide to debris flow and then from debris flow to bed-load transport; and (3) the development of an experimental debris-flow research facility for evaluating the rheological parameters and material constants of debris flow. Significant results obtained from tasks (1) and (2) have been the formulation of a generalized viscoplastic fluid (GVF) model and the subsequent development of a general routing model based on the GVF model. A number of journal papers on the GVF model were published. Efforts made in task (3) have resulted in substantial improvement on the U. S.Geological Survey debris-flow research facility in the University of California, Berkeley. Installed in the facility is an automatic control and data acquisition system which facilitates the control and operation of the "ring-shear" apparatus and the "conveyor-belt" flume as well as fast data processing and analysis. Numerous "ring-shear" experiments were conducted on "dry" glass beads of various uniform sizes, while major modifications were made on the "conveyor-belt" flume. The second phase of a joint research contract with the University of California, Berkeley, continued.

Chen, C. L., 1987, Discharge and depth behind a partially breached dam: 1987 National Conference on Hydraulic Engineering, American Society of Civil Engineers, Williamsburg, Va., 1987, Proceedings, p. 648-654.

Chen, C. L., 1987, Comprehensive review of debris flow modeling concepts in Japan in Costa, J. E. and Wieczorek, G. F., ed., Debris Flows/Avalanches: Process, Recognition, and Mitigation, Reviews in Engineering Geology, v. 7, Geological Society of America, Boulder, Colorado, p. 13-29.

Chen, C. L., 1988, Generalized viscoplastic modeling of debris flow: Journal of Hydraulic Engineering, American Society of Civil Engineers, v. 114, no. 3, p. 237-258.

Chen, C. L., 1988, General solutions for viscoplastic debris flow: Journal of Hydraulic Engineering, American Society of Civil Engineers, v. 114, no. 3, p. 259-282.

Chen, C. L., 1988, Issues in debris flow research: personal views: U.S. Geological Survey Water-Supply Paper Series "Selected Papers in the Hydrologic Sciences" 2340 (in press).

WR197 MODELING PRINCIPLES

TITLE: Mathematical Modeling Principles

PROJECT NUMBER: WR 73-197

LOCATION: Topical Research

PROJECT CHIEF: Bennett, James P.

HEADQUARTERS OFFICE: Menlo Park, CA

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 modeling the transport of sediments, including mudflows and hyperconcentrations such as occur after a natural disaster like volcanic eruptions or damn failures.

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

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

PROGRESS: The nutrient and sediment budget chapters for the final report on the Potomac Study were completed. Also completed were the introduction, summary and conclusions, and editing of all contributed sections of the final Potomac Study report. Literature review was completed and initial design was begun for a sediment transport model which includes co-transport and reactions of sorbed constituents for bed material and wash load.

Appendix I. Research Projects Listed for Each Water Resources Division Region

Appendix II. Project Chiefs of the Water Resources Research Program

PROJECT CHIEF	PROJECT SHORT TITLE	PROJECT NUMBER	PAGE
Andrews, Edmund D.	Hydrological-Biological Interactions	CR273	56
Averett, Robert C.	Ecology of Lakes and Streams	CR312	12
Back, William	Chemical Constituents of Water	NR034	75
Baedecker, Mary Jo	Organic Degradation	NR129	88
Baltzer, Robert A.	Numerical Simulation	NR019	204
Barnes, Ivan	Geochemistry of Geothermal Systems	WR080	98
Bencala, Kenneth E.	Flow and Geochemical Interactions	WR187	226
Bennett, James P.	Modeling Principles	WR197	231
Benson, Larry V.	Arid Regions Climate and Chemistry	CR207	168
Bredehoeft, John D.	Wells-Strain Meters	WR176	144
Bricker, Owen P.	Trace Metals and Nutrients	NR109	189
Brown, Charles E.	Surface Geophysics and Hydrology	NR130	130
Callender, Edward	Sed.-Water Exchange of Nut./Metals	NR065	183
Campbell, William J.	Ice Modeling and Remote Sensing	WR064	215
Carter, Virginia P.	Wetland Studies	NR090	15
Chen, Cheng-lung	Fluvial Mechanics	WR194	229
Cheng, Ralph T.	Hydrodynamics of Tidal Estuaries	WR140	219
Chiou, Cary T.	Sorption and Partition Phenomena	CR283	70
Claassen, Hans C.	Geochemical Kinetics Studies	CR189	162
Cleveland, Jesse M.	Transuranium Research	CR223	66
Cloern, James E.	Estuarine Plankton Dynamics	WR164	31
Conomos, T. John	Polaris Operations	WR156	221
Constantz, James E.	Temperature Effects, Unsat. Zone	WR193	153
Cooley, Richard L.	Simulation of Subsurface-Water Flow	CR191	118
Coplen, Tyler B.	Isotope Fractionation	NR064	81
Davis, James A., III	Solute Partitioning	WR065	96
Eberl, Dennis D.	Clay-Water Reactions	CR276	68
Emmett, William W.	Bedload Transport Research	CR187	52
Feder, Gerald L.	Water Quality and Health	NR132	90
Getzen, Rufus T.	Hydrologic Analysis of Petrofabrics	WR171	143
Glenn, Jerry L.	Estuary Sedimentation/Eutrophication	CR266	54
Godsy, Edward M.	Organic Chemicals in Subsurface	WR068	23
Goerlitz, Donald F.	Chemistry of Aquatic Organic Matter	WR189	105

PROJECT CHIEF	PROJECT SHORT TITLE	PROJECT NUMBER	PAGE
Goldberg, Marvin C.	Chemistry of Sediment Surfaces	CR199	164
Gorelick, Steven M.	Models for Ground-Water Management	WR178	145
Grove, David B.	Ground-Water Quality Modeling	NR139	133
Grove, David B.	Leopold Operations	NR143	214
Harvey, Ronald W.	Bacteria-Contaminant Interactions	WR191	41
Hem, John D.	Chemistry of Hydrosolic Metals	WR076	195
Herkelrath, William N.	Nonisothermal Multiphase Flow	WR179	147
Hsieh, Paul A.	Hydrology of Fractured Rocks	WR184	151
Ingebritsen, Steven E.	Heat and Mass Transport--Cascades	WR121	140
James, Ronald V.	Unsaturated Zone Solutes	WR036	94
Jones, Blair F.	Mineral-Water Interaction in Saline Environments	NR020	73
Kennedy, Vance C.	Solute Transport at Low Flow	WR044	193
Kharaka, Yousif K.	Geochemistry of Geopressured Systems	WR139	101
Kipp, Kenneth L.	Solute-Transport Simulation	CR292	122
Konikow, Leonard F.	Transport Modeling -- Saturated Zone	NR120	128
Kraemer, Thomas F.	Radioisotopes in Ground Water	NR138	92
Kuwabara, James S.	Solute Transport Involving Biota	WR190	38
LaBaugh, James W.	Hydrol-Biol Geochem Interactions	CR293	8
Lai, Vincent C.	Computational Hydraulics	NR096	206
Landa, Edward R.	Uranium Mill Tailings	NR092	185
Landwehr, Jurate M.	Regional Hydrologic Processes	NR133	212
Leavesley, George H.	Rainfall-Runoff Modeling	CR228	198
Leenheer, Jerry A.	Comprehensive Organic Analysis of Water	CR285	178
Leland, Harry V.	Toxic Substances: Aquatic Ecosytems	WR137	27
Lovley, Derek R.	Microbial Geochemical Models	NR136	17
Luoma, Samuel N.	Trace Elements Availability in Sediments	WR125	25
Malcolm, Ronald L.	Organic Hydrogeochemistry	CR046	156
Mariner, Robert H.	Western U.S. Geochemistry	WR165	103
Mayo, Lawrence R.	Alaska Glaciology	WR175	222
Mcknight, Diane M.	Organic-Trace Metal Interactions	CR286	6
Meade, Robert H.	Sediment in Rivers	CR102	48
Meade, Robert H.	Mississippi River Sediment Pollutants	CR309	59
Moench, Allen F.	Energy Transport in Ground Water	WR127	142

PROJECT CHIEF	PROJECT SHORT TITLE	PROJECT NUMBER	PAGE
Neuzil, Christopher	Cretaceous Shale Hydrology	NR035	125
Nichols, Frederic H.	Estuarine Benthic Comm. Dynamics	WR192	43
Nordstrom, Darrell K.	Trace Element Partitioning	WR128	99
Oremland, Ronald S.	Microbial Biogeochemistry	WR174	34
Osterkamp, Waite R.	Sediment Impacts from Disturbed Lands	CR311	60
Paillet, Frederick L.	Borehole Geophysics	CR140	116
Pereira, Wilfred E.	Organic Contaminants and Water Quality	CR278	170
Peterson, David H.	Geochem Rivers and Estuaries	WR046	21
Phipps, Richard L.	Plant Growth and Hydrology	NR027	13
Plummer, Leonard N.	Modeling Mineral-Water Reactions	NR056	79
Rathbun, Ronald E.	Organic Substances in Streams	CR301	202
Reddy, Michael M.	Corrosion by Wet Precipitation	CR284	176
Rees, Terry F.	Colloid Geochemistry	CR296	180
Rubin, Jacob	Infiltration and Drainage	WR024	135
Rubin, Jacob	Unsaturated Zone Theory	WR180	149
Schaffranek, Raymond W.	Modeling of Hydrodynamic Systems	NR104	208
Shapiro, Allen M.	Transport in Fractured Rock	NR134	131
Simon, Nancy S.	Speciation of Metals	NR135	191
Slack, Keith V.	Limnology: Benthic Communities	WR012	19
Smith, Richard L.	Microbial Geochem of Organic Matter	CR295	10
Sorey, Michael L.	Modeling Geothermal Systems	WR102	137
Sorey, Michael L.	Geothermal Coordination	WR108	139
Stallard, Robert F.	Sed.-Water Chem. in Large Rivers	CR313	63
Stevens, Herbert H., Jr.	Sediment Transport Phenomena	CR098	46
Sundquist, Eric T.	Geochemical Carbon Fluxes	NR099	187
Tasker, Gary D.	Regression and Data-Network Design	NR125	210
Taylor, Howard E.	Analytical Chemistry of Inorganics	CR282	173
Teasdale, Warren E.	Drilling Techniques	CR103	114
Thorstenson, Donald C.	Chemical Models	NR093	84
Triska, Frank J.	Biota-Solute Transport Interface	WR186	36
Troutman, Brent M.	Errors Analysis	CR279	200
Turner, Raymond M.	Vegetation Ecohydrology	WR145	29
Voss, Clifford I.	Subsurface Transport Phenomena	NR089	126

PROJECT CHIEF	PROJECT SHORT TITLE	PROJECT NUMBER	PAGE
Walters, Roy A.	Analysis and Modeling of Transport Proc	WR183	224
Weeks, Edwin P.	Unsaturated Zone Field Studies	CR200	120
Wershaw, Robert L.	Organic Polyelectrolytes	CR132	158
White, Arthur F.	Geochemistry at Mineral Surfaces	WR196	107
Williams, Garnett P.	Channel Morphology	CR105	50
Winograd, Isaac J.	Paleoclimatology and Aquifer Geochem	NR041	77
Winter, Thomas C.	Hydrology of Lakes	CR090	112
Wood, Warren W.	Ground-Water Dispersion	NR122	86

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