NATIONAL RESEARCH PROGRAM OF THE WATER RESOURCES DIVISION U.S. GEOLOGICAL SURVEY, FISCAL YEAR 1989

U.S. Geological Survey
Open-File Report 91-67

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OF THE

WATER RESOURCES DIVISION

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Compiled by
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U.S. Geological Survey
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THE NATIONAL RESEARCH PROGRAM OF THE WATER RESOURCES DIVISION, U.S. GEOLOGICAL SURVEY FISCAL YEAR 1989

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, the scope of their activity, and the emphasis of current study are listed below:

(1) ECOLOGY--Concerns 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, and 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 range from ground waters to lakes, rivers and estuaries and from coastal wetlands to forests and deserts.

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

(3) GROUND-WATER CHEMISTRY--Concerns inorganic, organic, and biochemical reactions affecting water quality in relation to mineralogy, geochemistry, and hydrology of 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 of behavior inorganic and organic solutes on particulate surfaces, the kinetics of silicate and carbonate mineral dissolution and crystal growth, isotopic fractionation in mineral-water-gas systems, the speciation of transuranium elements in ground water, the exchange properties of clays, and the thermodynamics of solubility and coprecipitation phenomena. Field studies involve controls of mineral-water-gas reactions in a wide variety of hydrochemical environments including shallow ground-water systems, regional aquifer systems, deep sedimentary basins and subsurface brines, geothermal systems, freshwater-saltwater interfaces, and the unsaturated zone. Studies include investigations of the degradation of organic matter and attenuation of toxic metals in environmentally stressed hydrochemical environments, relations between water quality and human health and disease, and physical and chemical processes affecting dispersion of dissolved solutes. Extensive applications of isotopic data are made to identify water sources, cross-formational

leakage, water age, paleoclimatic conditions, and reactants and products in the ground-water environment. Current modeling research focuses on the speciation of metals and other dissolved solutes in natural and contaminant waters, prediction of the thermodynamic properties of mineral-water reactions in ground-water systems, including brines and other highly saline fluids, and prediction of chemical and isotopic evolution in water-rock systems, and age-dating ground water.

(4) GROUND-WATER HYDROLOGY--Focuses on techniques for evaluating, understanding, and managing ground-water resources. Research into the role of the unsaturated zone is being conducted to provide information needed to evaluate ground-water conservation and management practices, such as artificial recharge, phreatophyte control, and the reduction of evapotranspiration. Currently, investigations of land subsidence are underway as are studies to determine how fracture zones, permeability distributions, and geothermal conditions affect, or are affected by, subsurface hydrologic processes. Comprehensive studies in borehole geophysics are being conducted to improve the resolution and effectiveness of these subsurface techniques. Efforts also are being made to develop new and to refine existing two- and three-dimensional models for use in understanding flow and solute transport in porous media in both the saturated and unsaturated zones. Parameter-estimation techniques to enhance and assess model accuracy also are being developed.

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

(6) SURFACE-WATER HYDROLOGY--Stresses studies to 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 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 uses 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; the areal distribution of hydrologic information; and 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 people that encroach 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 the presence of snow and ice affects climate, water supply, and (or) safety.

This report, one in a series of annual reports, provides current information about the NRP during fiscal year 1989. 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 1989. Bibliographic information is included with each project summary in the form of reports published from May 1988 through June 1989.

The projects headquartered in each WRD Region are listed in Appendix A, 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's short title, and the page number of the project summary. Appendix B is an alphabetic list of the Project Chiefs of all projects included in this volume, the project's 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 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 in natural waters can control the biogeochemistry of trace metals and other solutes and can influence ecological processes in lakes and streams. The nature and reactivity of the dissolved organic material is, in turn, influenced by biological, chemical, and physical processes in the aquatic environment. Recent advances in isolating and characterizing different fractions of dissolved organic carbon (DOC) and in measuring rates of microbial processes can be used to advance the understanding of the dynamic relations among aquatic biota and dissolved organic material and trace metals in different environments.

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

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

PROGRESS: A study of an ombrotrophic bog showed that the main source of DOC was the upper productive layer of sphagnum mat. A subsequent field study of the relation between trace-metal deposition and precipitation in the bog is underway. A study of the temporal and spatial dynamics of trace metals and natural organics in a mountain stream system has shown that (1) photoreduction of hydrous iron oxides is an important control on iron chemistry and (2) DOC is sorbed by hydrous metal oxides. A study of polar desert lakes in Antarctica is being conducted through the National Science Foundation, (NSF)-Division of Polar Programs. Microbially derived dissolved fulvic acids from two lakes in the Taylor Valley, Victoria Land, Antarctica, have been characterized. These lake ecosystems are comprised of established algal and bacterial populations and receive no inputs of organic material from the barren polar desert landscape. The increased concentration of fulvic acid with depth and the similar characteristics of fulvic acids from different depths indicate that these compounds are predominantly produced in the lake sediments and diffuse upward. In comparison with fulvic acids from other environments, these microbial end-member fulvic acids had low carbon-to-nitrogen atomic ratios (19-25) and a low but well-defined content of sp^2- hybridized carbons (15 percent), and were similar to marine fulvic acids.

REPORTS PUBLISHED:

McKnight, D.M. and Bencala, K.E., 1988, Diel variations in iron chemistry in an acidic stream in the Colorado Rocky Mountains, U.S.A: Arctic and Alpine Research, v. 20, no. 4, p. 428-500.

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.

McKnight, D.M., Miller, C., Smith, R.L., Baron, J., and Spaulding, S., 1988, Phytoplankton populations lakes in Loch Vale, Rocky Mountain National Park, Colorado--sensitivity to acidic conditions and nitrate enrichment: U.S. Geological Survey Water-Resources Investigations Report 88-4115, 102 p.

McKnight, D.M., Thorn, K.A., and Wershaw, R.L., 1988, Rapid changes in dissolved humic substances in Spirit Lake and South Fork Castle Lake, Washington: Limnology and Oceanography., v. 33, no. 6 (part 2), p. 1527-1541.

Kimball, B.A., Bencala, K.E., and McKnight, D.M., in 1989, Research on metals in acid mine drainage in the Leadville, Colorado, area, in Mallard, G.E., and Ragone, S.E., eds., U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the Technical Meeting, Phoenix, Arizona, September 26-30, 1988: U.S. Geological Survey Water-Resources Investigations Report 88-4220, p. 65-70.

Kimball, B.A. and McKnight, D.M., 1989, Metal partitioning and photoreduction of iron in filtrates of acid streamwater, St. Kevin Gulch, near Leadville, Colorado, in Mallard, G.E., and Ragone, S.E., eds., U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the Technical Meeting, Phoenix, Arizona, September 26-30, 1988: U.S. Geological Survey Water-Resources Investigations Report 88-4220, p. 93-100.

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 biogeochemical processes of the ecosystem 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 decision makers 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 further investigated in the field.

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

PROGRESS: One book chapter, one journal article, one USGS Open-File Report, and another Federal report (U.S. Fish and Wildlife Service

Technical Paper) were published. A report was written on the phytoplankton community of Williams Lake, Minnesota, 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, North Dakota, Crescent Lake refuge, Nebraska, and Williams Lake, Minnesota.

REPORTS PUBLISHED:

LaBaugh, J.W., 1989, Chemical characteristics of water in northern prairie wetlands, in van der Valk, A., ed., Northern prairie wetlands: Ames, Iowa, Iowa State University Press, p. 56-90.

LaBaugh, J.W., and Swanson, G.A., 1988, Algae and invertebrates in the water column of selected prairie wetlands in the Cottonwood Lake area, Stutsman County, North Dakota, 1984: U.S. Geological Survey Open-File Report 88-451, 96 p.

Swanson, G.A., Winter, T.C., Adomaitis, V.A., and LaBaugh, J.W., 1988, Chemical characteristics of prairie lakes in South-Central North Dakota-their potential for impacting fish and wildlife: U. S. Fish and Wildlife Service Technical Report 18, 44 p.

Winter, T.C., LaBaugh, J.W., and Rosenberry, D.O., 1988, 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, p. 1209-1214.

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 transformations in either pristine or contaminated environments. Within the context of in situ environmental conditions, the mechanisms, pathways, rates, and factors controlling carbon cycling by microorganisms are poorly understood; however, these particular processes can significantly affect the entire range of biogeochemical and geochemical processes occurring within the aquatic environment.

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

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

PROGRESS: Research efforts were focused upon carbon and nitrogen cycling by microorganisms at two field locations; a ground-water site (Cape Cod Hazardous Waste Site) in Massachusetts and a permanently stratified lake (Lake Fryxell) in Antarctica. (1) Closely-spaced multilevel sampling devices (approximately 300 feet on a horizontal axis) have been used to measure migration of the leading edge of the ammonium zone within the contaminant plume at the ground-water site. This detailed sampling of the rate of ammonium transport on a plumewide basis will be compared with earlier studies in which Kd values for ammonium sorption were estimated by means of bath experiments and small-scale forced-gradient tracer tests. The heterogeneity of the sands and gravels in the aquifer is reflected in the vertical profile of the ammonium front, which is moving at differential rates within the different layers. The results of this study will determine the applicability of small-scale tests towards predicting transport of certain nitrogen-containing species on a plumewide basis. (2) Laboratory studies were undertaken with a pure culture of a denitrifying bacterium to develop assay procedures for the specific enzymes involved with denitrification. It has been possible to measure the activities of selected enzymes in whole cells when they are placed in an artificial sand and gravel environment, that simulates an aquifer. The technique involves the use of a specific inhibitor to prevent the expression of any new enzyme(s) while not interfering with the action of the existing enzyme(s). When the technique has been adequately tested with cultures, it will be applied to environment samples. The expression of the various enzymes can be used to map regions in nitrate-contaminated ground water in which denitrification is occurring. (3) Biochemical processes controlling the production and mineralization of organic matter were examined in a permanently stratified, ice-covered lake in Antarctica. There are no higher plants in the lake's watershed, hence, it is a closed system with respect to the carbon cycle. The microbial processes primarily responsible for carbon cycling were restricted to fairly narrow, distinct zones within the water column of the lake. These zones were reflected in the depth profiles of the total microbial biomass and the metabolic state (total adenine nucleotide content) of the microbial community. Fluxes of dissolved organic carbon and particulate organic carbon across the oxic-anoxic interface and across the sediment-water interface were also important components that linked primary productivity to heterotrophic activity within the various zones of the lake.

REPORTS PUBLISHED:

Harvey, R.W., George, L.H., Smith, R.L., and LeBlanc, D.R., 1989, Transport of microspheres and indigenous bacteria through a sandy aquifer--results of natural and forced-gradient tracer experiments: Environmental Science and Technology., v. 23, p. 51-56.

McKnight, D.M., Miller, C., Smith, R.L., Baron, J., and Spaulding, S., 1988, Phytoplankton populations in lakes in Loch Vale, Rocky Mountain National Park, Colorado--sensitivity to acidic conditions and nitrate enrichment: U.S. Geological Survey Water-Resources Investigations Report 88-4115, 102 p.

Brooks, M.H., and Smith, R.L., 1989, Total adenylate and adenylate energy charge measurements from bacterial communities in ground water, in Mallard, G.E., and Ragone, S.E., eds., U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the Fourth Technical Meeting, Phoenix, Arizona, September 26-30, 1988: U.S. Geological Survey Water Resources Investigations Report 88-4220, p. 541-545.

Smith, R.L., Howes, B.L., and Duff, J.H., 1989, The use of tracer tests to measure the transport and consumption of methane in a contaminated aquifer, in Mallard, G.E. and Ragone, S.E., eds., U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the Technical Meeting, Phoenix, Arizona, September 26-30, 1988: U.S. Geological Survey Water Resources Investigations Report 88-4220, p. 167-175.

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 extraction of 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 also difficult also to separate natural from human-induced changes in aquatic ecosystems.

OBJECTIVE: Determine experimentally the effects that geomorphic changes, other physical changes, and chemical changes have on aquatic habitat and upon the distribution and abundance of aquatic organisms.

APPROACH: Select several stream sites above lakes and on 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.

PROGRESS: Two paired lakes, Williams and Shingobee near Walker, Minn., have been selected for a major interdisplinary research study. Some eighteen NRP scientists have submitted study proposals to work on the above lakes. Several lakes in coastal southern Oregon also will be considered as part of the IRI program. Stream-habitat work is underway in Yellowstone National Park, Denali National Park, and in the Catskill Mountains of New York.

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.

Slack, K.V., Ferreira, R.F., Averett, R.C., and Kennelly, S.S., 1988, Effects of spatial orientation of multiple plate artificial substrates on invertebrate colonization: Water Resources Bulletin, v. 24, no. 4, p. 781-789.

Peterson, D.A., Averett, R.C., and Mora, K.L., 1987, Water quality of Fremont and New Fork Lakes, western Wyoming--a progress report: U.S. Geological Survey Water Resources Investigations Report 86-4016, 55 p.

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 used to interpret hydrologic phenomena.

OBJECTIVE: Determine relations between characteristics of the hydrologic environment and periodic plant-growth phenomena. 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. Determine relations between tree growth and environmental pollutants (including heavy metals and atmospheric pollutants).

APPROACH: Collect data of growth responses of many species in numerous habitats to ascertain types of information about the hydrologic environment that are 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 and examine the botanical growth processes involved, (2) describe the relations 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: The element content of tree rings was used to calculate the hydraulic properties at a landfill in eastern Maryland where ground-water was contaminated. Transport rates of iron and chloride inferred from tree rings agreed with ground-water velocity estimated from aquifer tests and modeling. Retardation factors for iron and a minimum of hydraulic conductivity were similarly calculated. Additional studies were initiated in Rhode Island and at another contaminated site in Maryland. Growth trends of the U.S. Forest Service tree-ring data along a sulfur gradient starting in Minnesota, extending through Wisconsin, and ending in Michigan have been analyzed for indications of growth decline. No growth decline was noted for aspen, red pine, or balsam fir. An apparent growth decline in jack pine appears to be a natural phenomenon related to age. An apparent decline in some sugar maples appears unrelated to the sulfur gradient.

REPORTS PUBLISHED:

Phipps, R.L., and Field, M.L., 1989, Computer programs to calculate basal area increment from tree rings: U.S. Geological Survey Water-Resources Investigations Report 89-4028, 124 p.

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 the understanding of these ecosystems, information is needed 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, and 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) retardation of flow velocities, stabilization of bottom sediments, and slowing of erosion; and (4) oxygenation of the water and recycling of 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 poorly understood.

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 oxygen, and recharge and discharge relations on the western transition zone of Dismal Swamp; (2) collect data on ground water 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 the relation between plant success and other environmental factors.

PROGRESS: During 1988, submersed aquatic macrophytes continued to spread downstream in the tidal Potomac River. Belmont Bay and Pohick Bay continue to be unvegetated, probably because of insufficient light. It has been shown that the large beds of vegetation improve water clarity, uptake sediment nutrients, and increase dissolved-oxygen concentrations, pH, and temperature during the day. Hydrilla is slowly replacing the other species found in the river--it dominates most of the freshwater tidal reach between Gunston Cove and Alexandria. Results of previous work on the Great Dismal Swamp of Virginia and North Carolina continue to be published.

REPORTS PUBLISHED:

Rybicki, N.B., Anderson, R.T., and Carter, Virginia, 1988, Data on the distribution and abundance of submersed aquatic vegetation in the tidal Potomac Estuary, Maryland, Virginia, and the District of Columbia, 1987: U.S. Geological Survey Open-File Report 88-307, 47 p.

Carter, Virginia, Rybicki, N.B., Jones, R.C., Barko, J.W., Dresler, P.V., Hickman, R.E., and Anderson, R.T., 1988, Data on physical, chemical and biological characteristics of Hydrilla beds, mixed vegetation beds, and unvegetated sites in the tidal Potomac River, Maryland and Virginia: U.S. Geological Survey Open-File Report 88-709, 196 p.

Carter, Virginia, Barko, J.W., Godshalk, G.L., and Rybicki, N.B., 1988, Effects of submersed macrophytes on water quality in the tidal Potomac River, Maryland: Journal of Freshwater Ecology, v. 4, no. 4, p. 493-501.

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 water and ground water; (2) determine the physiological characteristics that control the rate and extent of microbial processes; and (3) develop mathematical models of the distribution of microbial processes in surface water and ground water.

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

PROGRESS: Aromatic compounds are the most common contaminants of ground water, and geochemical studies have indicated that Fe(III) may be an important oxidant of these aromatic compounds. Previous studies have indicated only abiological mechanisms for the oxidation of aromatic compounds with Fe(III). During this project, it was found that Fe(III)-reducing microorganisms have the capacity to oxidize a wide variety of aromatic contaminants including hydrocarbons, phenol, cresol, and aromatic acids. Furthermore, studies at the Ground-water Toxics Site in Bemidji, Minn. indicated that these microbially catalyzed reactions, not abiological reactions, are responsible for removing aromatic contaminants from ground water. These findings are important to basic microbiology, as they greatly expand the known physiological capabilities of Fe(III)-reducing microorganisms. The oxidation of toluene is especially exciting, as this is the first example of an organism of any kind that can anaerobically oxidize an aromatic hydrocarbon. Information on the metabolism of these organisms will eventually enable modeling of the factors controlling the rate and extent of contaminant removal in these systems and will aid in the development of bioremediation strategies for aquifers contaminated with aromatic compounds. (1) It was discovered that Alteromonas putrefaciens can obtain energy for growth by oxidizing organic compounds with the reduction of Fe(III) or Mn(IV). More importantly, this organism was found to couple the oxidation of hydrogen or formate to the reduction of Fe(III) or Mn(IV), thus providing a pure-culture model for important reactions in the decomposition of organic matter in Fe(III)- and Mn(IV)-reducing sediments. From these culture studies and earlier ones on the organism, strain GS-15, a conceptual was modeling for the oxidation of organic matter coupled Fe(III) or Mn(IV) reduction in sediments. (2) In the continuation of studies on the factors that result in the separation of different microbial respiratory processes into distinct zones, a study was conducted on the factors that result in the inhibition of iron reduction in the presence of manganese oxides. This had previously been proposed to be the result of preferential reduction of manganese by iron-reducing organisms. However, a combination of sediment and culture studies showed that the chemical oxidation of ferrous iron by manganese oxides is the major factor preventing net Fe(III) reduction. (3) Mossbauer spectroscopy, low-temperature magnetic analyses, and high-resolution transmission electron microscopy revealed that the magnetite produced by the dissimilatory iron-reducer, GS-15, is a mixture of super-paramagnetic and single-domain magnetite and has a morphology distinctly different than that of the magnetotactic bacteria. These results are significant, as they provide distinguishing characteristics that will aid in determining the source of magnetite in sediments. This is important for interpreting magnetic data for studies of soil erosion and transport into aquatic systems. (4) Progress was made in making in situ measurements of dissolved hydrogen gas in sedimentary environments. Evaluation of a number of techniques demonstrated the necessity for hydrogen gas measurement be made in such a way as to prevent rapid ongoing hydrogen production in sediments. Equilibrator techniques were found to be the best method. Field measurements with the equilibrator were consistent with earlier results from laboratory studies and supported the hypothesis that concentrations of dissolved hydrogen gas indicate the the terminal electron-accepting process taking place in a given environment.

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Lovley, D.R., and Goodwin, S., 1988, Hydrogen concentrations as an indicator of the predominant terminal electron accepting reactions in aquatic sediments: Geochimica Cosmochimica Acta, v. 52, p. 2993-3003.

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

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

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

PROGRESS: Invertebrate drift was collected in the upper Snake River (pH 3.5 to 4.3) and Deer Creek (pH 6.5 to 8.0) about 100 meters above the confluence of these second-order streams in the Rocky Mountains of Colorado. Nested drift nets of 425-, 209- and 106-um (micrometer) mesh were used to study mesh-size effects on collection of Chironomidae larvae. Average chironomid drift densities in Deer Creek were 15 times higher than those in acidic Snake River. The number of taxa collected by the 425-, 209- and 106-um nets were 21, 42, and 54 in Deer Creek and 7, 19, and 31 in Snake River. Different taxa were numerically dominant in the two streams and, within each stream, in the catches of the three nets. However, individuals of taxa that made up 70 percent of the total drift density in both streams were predominantly retained by the 106-um mesh after passing through the larger mesh sizes. Twenty-four taxa were collected by the 106-um nets and not by the other nets, but all except one (Pagastia II from Deer Creek) were rare. Although exposed to the same species pool, the streams had very different benthic communities, as expressed by their different drift assemblages.

REPORTS PUBLISHED:

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Tilley, L.J., 1989, Diel drift of Chironomidae larvae in a pristine Idaho mountain stream: Hydrobiologia, v. 174, p. 133-149.

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 aphysical processes and rates (PAR) that control changes in water and sediment chemistry in river, estuary, and coastal-ocean systems are poorly defined. Such understanding 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 and 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 systems by comprehensive field (shipboard and in situ instrumentation) and numerical-simulation methods. Analyze systems variability on various scales as data become available; for example, interannual variability (primarily climaterelated), long-term trends (human factors), and seasonal and short-term source-sink processes (photosynthesis/mineralization).

PROGRESS: Interannual variability in atmospheric flow exerts a strong influence on regional precipitation and, consequently, on streamflow. A good example is the effect of the central North Pacific Low in winter, which is linked by various mechanisms to streamflow anomalies in Hawaii, coastal Alaska, and the northwestern United States. Streamflow in other regions in the West, including California, although not strongly coupled to conditions in the central North Pacific, responds to other characteristic atmospheric anomaly patterns. Some of the most significant streamflow fluctuations are multiyear periods during wet or dry regimes characterized by repeated occurrences of anomalous atmospheric flow patterns. To the extent that stream chemistry is related to flow, climatic effects can also be linked to anomalous trends in stream chemistry. Dissolved-solids data from previous studies show correlations with streamflow fluctuations and, further, with atmospheric patterns. Selected examples seem to demonstrate that a series of dry years in the normally wet Northwest shifts the stream chemistry trends towards those of the arid Southwest. Evidence indicates that these effects are integrated over time, so that the relation of water chemistry to streamflow changes from the beginning of a dry period to the end of that period. Thus, caution should be used in identifying the origin of "changes" in stream chemistry as human induced, given the possibility of low-frequency, natural changes caused by climatic variability.

REPORTS PUBLISHED:

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Schemel, L.E., Ota, A.Y., Hager, S.W., and Swithenbank, A.M., 1989, Sources of dissolved and particulate substances to the Sacramento River near Sacramento, California, summer, 1985: U.S. Geological Survey Open-File Report 89-45, 62 p.

Schemel, L.E., Ota, A.Y., Harmon, J.G., Shay, J.M., and Adorador, R.N., 1988, Benthic macrofauna and ancillary data for San Francisco Bay, California, March to November 1987: U.S. Geological Survey Open-File Report 88-192, 73 p.

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 that control the persistence and movement of these compounds are not well understood. A better understanding is necessary to aid in construction of models to predict movement and fate of pollutants in the subsurface and for design of control and abatement techniques.

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

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

PROGRESS: The movement and fate of the major water soluble compounds of creosote are being studied in the laboratory and at the USGS Hazardous Waste Study Site at Pensacola, Fla. Characteristics of adsorption onto aquifer material have been determined for 12 different creosote derived compounds by use of a novel high-pressure liquid-chromatography technique. The kinetics and pathways of transformation under methanogenic conditions have been determined for six compounds in laboratory microcosms. A pathway, as yet unreported, has been demonstrated where the initial microbial attack can occur on either ring of two-ring nitrogen-, sulfur-, and oxygen-containing heterocyclic compounds. Solute-transport models describing the movement and fate of selected creosote compounds and based on the parameters determined in the laboratory are being prepared.

REPORTS PUBLISHED:

Godsy, E.M., and Grbic'-Galic', Dunja, 1989, Biodegradation pathways for benzothiophene in methanogenic microcosms, in Mallard, G.E, and Ragone, S.E., eds., U.S. Geological Survey Toxic Substances Hydrology--Proceedings of the Technical Meeeting, Phoenix, Arizona, September 26-30, 1988: U.S. Geological Survey Water-Resources Investigations Report 88-4220, p. 559-564.

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

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

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

PROGRESS: Completed papers on metal dispersal in sediments of Clark Fork River, Montana, interaction of growth and exposure in determining metal burdens in estuarine clams, and management of hazardous waste from mineral extraction. Developed time series calculations describing effects of salinity and river inflow on fate and effects of metals in North San Francisco Bay, California, and completed a paper. Conducted field work on effects of acid drainage on benthos and trout in Blackfoot River, Montana, and completed a paper. Began field work to assess influence of metal concentrations in interstitial waters on metal bioavailability; this includes methods for collecting interstitial waters and a new method for concentrating metals from solution. Continued collection and synthesis of data concerning use of stream benthos as geochemical sentinel organisms, including specific experiments to determine the influence of undigested stomach contents on metal burdens. Completed experiments modifying sediments and determining effects on bioavailability of silver. Began study of petroleum-hydrocarbon signatures in North San Francisco Bay, California. Interpreted existing U.S. Environmental Protection Agency (EPA) data on organochlorine concentrations in fish tissues in Illinois basin and wrote informal report for the National Water Quality Assessment Program (NAWQA) team; continued to participate in development of biological methodology for NAWQA. Began developing new protocol for determining metal-assimilation efficiencies from different food types, employing much shorter experiments than have been done in the past.

REPORTS PUBLISHED:

Johns, C., and Luoma, S.N., 1988, Selenium accumulation in benthic bivalves and fine sediments of San Francisco Bay, the Sacramento-San Joaquin Delta, and selected tributaries: Estuarine, Coastal and Shelf Science, v. 27, p 381-396.

Luoma, S.N., and Phillips, D.J.H., 1988, Distribution, variability and impacts of trace elements in San Francisco Bay: Marine Pollution Bulletin, v. 19, p. 413-425.

Hostettler, F.D., Rapp, J.B., Kvenvolden, K.A., and Luoma, S.N., in press, Biogenic and anthropogenic organic markers as source discriminants and sediment transport indicators in South San Francisco Bay, California: Geochimica et Cosmochimica Acta, v. 53, no. 7.

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

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 for 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, including 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 (physicochemical and biological) influencing responses of natural aquatic communities.

PROGRESS: Studies were conducted on the effects of irrigation wastewater and subsurface drainage on aquatic communities of the San Joaquin River and its tributaries in California. Bioavailable Se concentrations, as indicated by accumulation in the bivalve *Corbicula*, varied directly with the dissolved Se concentration during the primary irrigation season, whereas tissue concentrations of As varied directly with the acid-extractable (pH 2) As:Fe ratio of suspended matter. Bioavailable concentrations of Cd, Cu, and Hg were enriched in several of the tributaries. Water hyacinth, *Eichhornia*, was shown to have potential as a bioindicator of water quality (that is, in assessment of the distribution of bioavailable trace elements). The species composition of the benthic-invertebrate community in areas of stable substrate was found to be strongly related to the concentration of dissolved solids in river water. The distributions of invertebrate taxa in sandy sediments was most closely related to the particle-size distribution of sediments. Studies were also initiated on the benthic ecology of the Yakima River, Washington. These ecological studies may provide a framework for examining spatial variations in biological communities in the National Water Quality Assessment Program (NAWQA).

REPORTS PUBLISHED:

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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 water-table 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 affect 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 regional water quantity and quality, 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 serial 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: (1) J.L. Betancourt is studying a disjunct stand of pinon pine in northeastern Colorado in collaboration with the University of Colorado. The U.S. Geological Survey provides packrat-midden analysis and University of Colorado contributes genetic and dendrochronologic analyses. This pine stand became established about 400 years ago by long-distance dispersal of seeds from populations 250 kilometers to the south. Preliminary results show that the 5-square-kilometer stand probably resulted from intentional plantings by Indians. In a related study, isolated stands of limber pine on the Great Plains (Pawnee Buttes, Colorado) were examined. Trees in these scarp woodlands are only one or two centuries old. The genetic homogeneity of the stands indicates recent arrival, but the fossil record shows that limber and ponderosa pine have occupied these sites at various times over the past two to three millennia. The fossil, genetic, and demographic evidence indicates that these woodlands are subject to catastrophic losses, possibly because of fire, and readily reestablish by dispersal of seeds from the Rockies. Betancourt is also studying the dynamics of shrub invasion in the central Rio Grande Valley of New Mexico. At the University of New Mexico's Sevilleta Long Term Ecological Project Site, pinon pine, one-seed juniper, and creosote bush have all undergone marked population changes within the past millennium. These vegetation changes may accelerate with projected climate changes associated with greenhouse warming. In another packrat-midden study, new methods are being developed for estimating rates of cliff retreat in the Bandelier Tuff at Los Alamos National Laboratory, New Mexico. This research bears upon the potential release of buried radioactive wastes after chronic erosion. (2) Five permanent saguaro plots in southern Arizona were examined by R.M. Turner, T.L. Burgess, and J.E. Bowers to determine rates of establishment and mortality of this cactus. Some of the populations have been relatively stable since they were first examined in 1960; others have shown a large recruitment surge in recent years. Findings show that, in general, saguaro populations are actively reproducing and, contrary to recent speculation, the species is not facing imminent decline.

REPORTS PUBLISHED:

Bowers, J.E., in press, A debt to the future -- scientific achievements of the Desert Laboratory, Tumamoc Hill, Tucson, Arizona: Desert Plants, v. 10

Betancourt, J.L., in press, Late Quaternary biogeography of the Colorado Plateau, in Betancourt, J.L., Van Devender, T.R., and Martin, P.S., eds., Packrat middens, late Quaternary paleoecology of the arid West: Tucson, Ariz., University of Arizona Press.

Webb, R.H., and Betancourt, J.L., in press, The spatial distribution of radiocarbon ages from packrat middens, in Betancourt, J.L., Van Devender, T.R., and Martin, P.S., eds., Packrat middens, late Quaternary paleoecology of the arid West: Tucson, Ariz., University of Arizona Press.

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

PROGRESS: Published articles on the following topics: (1) quantitative relations between phytoplankton population turnover rate and availability of light in an estuary; (2) distributions of trace metals in the urbanized South San Francisco Bay estuary (with J. Kuwabara and others); (3) spatial and temporal variability of conservative (salinity) and nonconservative constituents (chlorophyll, suspended sediments) in a coastal-plain estuary; (4) use of the ^{14}C method for measuring primary productivity (chapter in a U.S. Geological Survey Techniques of Water-Resources Investigations report); and (5) an overview of interdisciplinary research activities in Tomales Bay, California. Completed a field study of vertical density structure at very small spatial scales (millimeters) in South San Francisco Bay; these measures will be analyzed to characterize vertical mixing intensity as a function of tidal energy. Completed an annual study of phytoplankton biomass and productivity after 2 years of extreme drought in northern San Francisco Bay (production was only 20 percent of that observed in normal water years). Initiated field activities at WRD's new Interdisciplinary Research Initiative site in Minnesota. Continued development of a laboratory flume; progress included use of a laser-Doppler anemometer to characterize the flow field under a variety of velocities, use of a unialgal culture for measuring grazing rates of filter-feeding clams in simulated tidal flows, and the first demonstration that feeding rates of clams are variable and functions of freestream velocity. Added a 12th year to a study of hydrography/plankton ecology in South San Francisco Bay.

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Powell, T.M, Cloern, J.E., and Huzzey, L.M., in press, Spatial and temporal variability in South San Francisco Bay, I. Horizontal distributions of salinity, suspended sediments, and phytoplankton biomass and productivity: Estuarine, Coastal and Shelf Science, v. 28.

Cloern, J.E., Powell, T.M., and Huzzey, L.M., in press, Spatial and temporal variability in South San Francisco Bay, II. Temporal changes in salinity, suspended sediments, and phytoplankton biomass and productivity over tidal time scales: Estuarine, Coastal and Shelf Science, v. 28.

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: Microorganisms 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 are poorly understood. In addition, microbes are geochemically active in environments representing biological extremes, such as volcanoes, hot springs, spreading centers, and hypersaline waters, and at extremes 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 in aquatic environments that do not represent biological extremes.

APPROACH: Study pathways of biogeochemical transformations mediated by microorganisms in the laboratory with materials taken from the environment (for example, sediments). Conduct biochemical experiments with isolated cultures of microorganisms 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: Selenate respiration was discovered and an in situ assay devised. This technique has been used to determine Michaelis-Menten kinetics in a wide diversity of sediment types (freshwater through extremely hypersaline), as well as in the subsurface. Work now continues on the cultural physiology of isolates.

Demethylation of methyl mercury results in production of carbon dioxide (previously undescribed) and methane. Results indicate involvement of methanogens and sulfatereducers. Previous investigators inferred only a dealkylkation/detoxification reaction; a C-1however, results from this ivestigation has led to hypothesis of substrate anology for oxidation. Demethylation of arsenic (cacodylic acid; trimethylarsine) is also oxidation and is being studied. Dissimilatory arsenate reduction will be investigated.

Diazotrophic dynamicsin in Mono Lake have been investigated, as have the chemical aspects of meromixis and the nannoplankter abundance/productivity. Further work is planned to quantify sulfatereduction and methanogenesis (precursors also) in this lake as well as in Big Soda and Soap Lakes. Gas exchange also will be studied by use of conservative tracers (sulfur hexaflouride, tritium, and so forth) and a nonconservative tracer (methane).

Studies have been conducted on the biogeochemistry of radiative trace gases. With regard to methane, a synthesis review of atmospheric methane was written with R. Cicerone. A paper on methane flux from lakes was published with L. Miller. These and other papers were given at an American Chemical Society meeting on methane (1987; Oremland, chairman) and have been published in "Global Biogeochemical Cycles".

REPORTS PUBLISHED:

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Cicerone, R., and Oremland, R.S., 1988, Biogeochemical aspects of atmospheric methane: Global Biogeochemical Cycles, v. 2, p. 299-328.

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Oremland, R.S., 1989, Present day activities of anaerobic bacteria and their relevance to future exobiological investigations: Advances in Space Research, v. 9, p. 127-136.

Oremland, R.S., Hollibaugh, J.T., Maest, A., Presser, T., Miller, L., and Culbertson, C., 1989, Selenate reduction to elemental selenium by anaerobic bacteria in sediments and culture--Biogeochemical significance of a novel, sulfate-independent respiration: Applied and Environmental Microbiology v. 55, p. 2333-2343.

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 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 poorly understood , 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 at background concentrations and with mixtures of conservative and nonconservative solutes injected into pristine and anthropogenically modified 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 that have high assimilative demand and can subsequently be passed to higher trophic levels (that is, carbon, nitrogen, phosphorous). Project orientation is to emphasize process rates rather than community structure. Cooperate with other projects interested in biogeochemical cycling and biotic-abiotic transport interactions.

PROGRESS: (1) A simulation model of algal uptake by A. Jackman, B. Kim (University of California at Davis), and F. Triska is being prepared for publication. The model couples estimates of nitrate-uptake rates by periphyton collected from instream flume studies to hydrologic models of Bencala (WRD, Menlo Park), Jackman, and Kim. Hydrologic data are fitted from an instream chloride injection to Little Lost Man Creek, Humboldt County, California. Biotic uptake rates are not fitted. Actual nitrate uptake is effectively simulated by the model. Two studies of the bacterial processes of nitrification and denitrification, respectively, from subsurface (hyporheic) flows at Little Lost Man Creek have been submitted for Director's Approval by F.J. Triska and J. Duff (this project). The reports indicate that nitrogen flux in the stream is a complex interaction between biota, the hydrology of subsurface exc hange flows, and sediment lithology. (2) D. Smith (WRD, Denver) and J. Duff found methane oxidation in aerobic and nitrate-enriched zones of an unconfined sand and gravel aquifer (at Otis Air Force Base, Massachusetts), with slightly higher rates in the aerobic zone Methane oxidation in the anaerobic zone was found in the areas exhibiting the highest denitrification rates, thus, methane oxidation may be coupled to nitrate reduction. (3) Depth profiles by D. McKnight, D. Smith, and G. Aiken (WRD, Denver) and J. Duff for ice-covered Antarctic lakes revealed constant increases in disssoved organic carbon (DOC), alkalinity, and specific conductance from just beneath the ice to the bottom of the lakes. In contrast, the cancentration of dissoved oxygen was very high in the upper waters, decreased dramatically at 8-9 meters, and was absent in the bottom waters. Productivity was restricted to narrow zones 2-4 m below the ice. Maximum heterotrophic activity occurred at 9-11 m. The sediments were the other major zone of heterotrophic activity in the lake and appeared to be the predominant source of DOC and other reduced compounds. (4) The Rio Salto, a swampy river in Costa Rica, was studied by F. Triska, J. Duff, and G. Zellweger (WRD, Menlo Park) and C. Pringle (University of California at Berkeley). Preliminary results indicate that denitrification was nitrate limited in organic-rich, "swampy" sediments. Nitrogen fixation and methanogenesis were observed in sediment slurries. It is likely that carbon dioxide is an important terminal electron acceptor in this stream environment. Assays of nutrient uptake at the ecosystem level were conducted by injection of nitrate, ammonium, DOC, and phosphate to either or both the Rio Salto and Rio Pantano, Costa Rica. Samples are currently being analyzed.

REPORTS PUBLISHED:

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Triska, F.J., Kennedy, V.C., Avanzino, R.J., Zellweger, G.W., and Bencala, K.E., in press, Retention and transport of nutrients in a third order stream in northwestern California -- channel processes: Ecology, v. 70.

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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 affects and is affected by biological activity. Therefore, understanding and quantifying solute interactions with biota can be important in developing accurate water-quality models. Although inorganic and organic complexation have been emphasized in previous toxicological studies in chemically defined media, it is clear that chemical processes suppressed in these experiments can be important in natural water systems. The effects of biological processes on solute uptake and transport need to be quantified and incorporated in transport models.

OBJECTIVE: Study transport of 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 with chemically defined particles and formulate a conceptual representation of the processes. Conduct culture experiments with 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 by means of various preparative techniques. Use chemically defined particles and unialgal cultures to describe processes controlling solute uptake and release by cells. Conduct laboratory culture experiments with 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: Arsenic-transport studies at Whitewood Creek, South Dakota, a stream affected by mining and having a longitudinally opposed dissolved arsenate and orthophosphate concentration gradient, are presently generating reports that have been submitted for journal publication or are in preparation. A dense, annual community of attached algae and submerged macrophytes quickly forms after snowmelt and remains throughout the summer months. Peak dissolved As (primarily arsenate) concentrations in the stream water also occur during this growth season. A study in cooperation with the Rapid City Subdistrict Office, as part of the Surface Water Toxics Hydrology Program, has examined the interactive effects of arsenate and orthophosphate on the periphyton-uptake characteristics for these two solutes. The following findings are believed to be noteworthy: (1) All test isolates exhibited some exclusion mechanism by which phosphate was preferentially taken up over arsenate or by which excessive cell-associated As was released; (2) initial uptake of both solutes appeared to follow a first-order time dependence; (3) although uptake-rate constants increased slightly with increased dissolved arsenate concentration, algae isolated from a site with elevated dissolved As had a significantly slower As rate of uptake than did the same species isolated from an uncontaminated site upstream; and (4) arsenic saturation by test algae at lower ambient concentrations relative to previous laboratory studies by others indicates another contributory factor toward the survival of Whitewood Creek isolates over the dissolved As concentration range along our 57-kilometer study reach (>70 micrograms per liter). Relations between physical characteristics (air and water temperature, photosynthetically reactive irradiance) and chemical characteristics (pH, As speciation, dissolved orthophosphate, specific conductiance, alkalinity) and photosynthetic activity (chorophyll-a, standing crop) were examined in this reach during the 1988 growth season with the aid of a data-logging device. Observed relations have been reported in a manuscript that is currently being [collegue] reviewed.

Background trace-metal concentrations in Lake Tahoe, California/Nevada and three inflowing tributaries were collected. Lake-water samples were collected from a nearshore (180-meter depth) and midlake (450 meter depth) station at five depths. Macronutrient, major-ion and adenosine triphosphate concentrations were also analyzed. Data indicate that the relative ordering of dissolved trace metals (Cu>>Ni similar to Zn>Cd) and metals in the particulate phase (Zn>Cu>Cd) may be explained in part by the relative stability of complexes of these metals with organic ligands (Cu>Ni>Zn>Cd). An empirical relation between dissolved and particulate trace-metal concentrations could not be determined because of the as yet small size of our data set. Dissolved and particulate concentrations were more variable between snowmelt sampling dates than between creeks. In a collaborative effort with Prof. Thomas Tisue of Clemson University, South Carolina, and the Tahoe Research Group, University of California at Davis, (1) sediment cores were taken from the midlake station to determine trace-metal concentrations and obtain an estimate of suspended-sediment settling rates; and (2) 1,000-liter water samples (collected from both stations at 30-meter depth) were processed with a tangential-flow filtration device to determine metastable cadmium-113 concentrations. Field data in combination with bioassay studies on lake water will allow better quantification of the delicate balance of limiting nutrients within this oligotrophic system. Initial lake data indicate that this balance is exhibited, in part, as interactive effects of trace metals and macronutrients on phytoplankton growth. Water-column trace-metal studies in San Francisco Bay have been published and have motivated two extended studies planned for next year.

REPORTS PUBLISHED:

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Chang, C.C.Y., Kuwabara, J.S. and Pasilis, S.P., in press, Trace metal concentrations of three tributaries to Lake Tahoe, California and Nevada, in Goldman, C.R., ed., Proceedings of the International Mountain Watershed Symposium, Tahoe, California, June 8-10, 1988: Proceedings.

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. Because of the persistence of some contaminants in the subsurface environment and because of increasing demands for both high-quality ground water and on-land disposal of toxic chemicals and radioisotopes, these interactions should remain important environmental problems for the next few decades. Because significant biotransformation/biodegradation of many environmental contaminants in aquifers and particle-laden surface waters can occur at particle surfaces, explanations for bacteria-contaminant interactions in such environments should take the presence of particles into account.

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

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

PROGRESS: An assay involving extraction and quantification of DNA associated with adherent bacteria in aquifer sediments was developed to allow estimation of particle-bound bacterial biomass in contaminated aquifer sediment. DNA from organically contaminated and uncontaminated aquifer sediments collected at the Groundwater Contamination Study Site at Otis Air Force Base (Massachusetts) has been extracted, purified, and stored for future research involving gene probing to delineated microbial community structure. Several small-scale, natural-gradient groundwater tracer-injection experiments were started and completed. A model was developed that describes transport of indigenous bacteria in the small-scale tests. It accounts for advection, dispersion, sorptivefiltration, physical heterogeneity, and retardation. Results of previous small-scale experiments were published. The preliminary phases of research involving the distribution and significance of subsurface protozoa at the Otis site were completed. Analyses were also completed for bacterial "signature" lipids in samples of aquifer material collected along chemical gradients at the Otis site.

Harvey, R.W., George, L.H., Smith, R.L., and LeBlanc, D.R., 1989, Transport of microspheres and indigenous bacteria through a sandy aquifer--results of natural and forced-gradient tracer experiments: Environmental Science and Technology, v. 23, p. 51-56.

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WR192	ESTUARINE BENTH IC 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, such communities 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 masks human-induced changes. In addition, estuarine benthic communities, often dominated by suspension feeders, have an unknown but potentially large controlling effect on phytoplankton biomass and can thus be important in limiting eutro-phication.

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 that 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 with transplanted animals and through laboratory experiments with individual species and intact infaunal communities in flumes that simulate changing field conditions.

PROGRESS: (1) During FY89, continued studies of the spread of the clam *Potamocorbula amurensis*, which was recently introduced into San Francisco Bay, California. Placed particular emphasis on intense quantitative sampling within the Suisun Bay area, in conjunction with the phytoplankton group (J. Cloern), to document spatial and temporal patterns of distribution, growth, and mortality. A major goal is to assess the possible role of this species in limiting phytoplankton biomass in the null zone area (Thompson/Nichols). Completed a report describing the introduction, growth, and spread of this new clam population in San Francisco Bay. This report (with J. Carlton from Univ. of Oregon, and Schemel) includes an analysis of mode and timing of introduction and discussion of the possible effects this clam will have on the bay's pelagic and benthic food webs. Began a report (with Schemel) describing how long-established patterns in the benthic community of northern San Francisco Bay (alternating normal and dry-weather community types) have been radically altered as a result of the arrival of the new clam. (2) After a long period of developing a recirculating seawater flume system, it was successfully demonstrated that grazing rates of "seeded" populations can be measured under a range of flow regimes. Initial flow-characterization measurements also were conducted (with colleagues from Stanford University and their laser doppler system). Presently working to more precisely define the hydrodynamics of flow in the flume (with B. Cole). Continuing the study of the relations between metal availability and reproduction in the clam Macoma balthica, with the goal of developing a stress marker (with Cain and Luoma). (3) Continued collection and analysis of benthos samples from Puget Sound, Washington, in a study of effects of long-term (decades) climate-related patterns and trends on benthic-community structure.

REPORTS PUBLISHED:

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Nichols, F. H., 1988, Long-term changes in a deep Puget Sound benthic community--local or basin-wide?: Puget Sound Research Conference, 1st, Proceedings: Puget Sound Water Quality Authority, v. 1, p. 65-71.

Nichols, F. H., Cacchione, D. A., Drake D. E., and Thompson, J. K., in press, Emergence of burrowing urchins from California continental shelf sediments--a response to alongshore current reversals?: Estuarine, Coastal and Shelf Science, v. 29.

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 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 function in a variety of other ways. As yet, the relations between pertinent hydraulic and sedimentologic variables are not completely understood. Hence, the extent to which important variables, particularly bed-form roughness and sediment transport, will change in response to natural or human-induced alterations to the flow regime cannot be predicted with desired reliability. As a result, optimum use 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 bedload transport. This problem is particularly acute in mined areas.

OBJECTIVE: Provide an improved understanding of sedimentation phenomena in alluvial streams and the response of such streams to imposed changes through the use of improved instrumentation. Consider the interrelations between bed-form characteristics and the transport of bedload and bed-material load.

APPROACH: Analyze existing data to relate bed-form characteristics to the conditions of flow and sediment transport. Develop one or more bed-load samplers to permit accurate measurements of bedload transport. 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. Analyze information to define criteria for predicting bed-form morphology and to provide a better under- standing of sediment-transport phenomena in sand and gravel-bed streams.

PROGRESS: Established a procedure for a moving-boat method to collect suspended-sediment samples and water-discharge data from the Mississippi River. Water-discharge data were verified by comparisons with data collected by conventional methods at selected sites.

REPORTS PUBLISHED:

Stevens, H.H., Jr., and Yang, C.T., in press, Summary and use of selected fluvial sediment-discharge formulas: U.S. Geological Survey Water-Resources Investigations Report 89-4026.

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 1,000 years. Understanding the movement and storage of sediment in rivers is important to navigation, flood control, and other aspects of river engineering, as well as to the prediction of the fate of contaminants absorbed on sediment particles.

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

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

PROGRESS: Two sampling cruises were completed on the Mississippi River between St. Louis and New Orleans. A resurvey of cross sections in Powder River, Montana, showed small to moderate amounts of channel change since last year. The total amount of channel change in Powder River in the 10 years since the flood of 1978 is of the same magnitude as the change that occurred during the few days of the flood itself.

REPORTS PUBLISHED:

Johnsson, M.J., Stallard, R.F., and Meade, R.H., 1988, First-cycle quartz arenites in the Orinoco River basin, Venezuela and Colombia: Journal of Geology, v. 96,no. 3, p. 263-277.

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Marron, D.C., in press, Physical and chemical characteristics of a metal-contaminated overbank deposit, west-central South Dakota, U.S.A.: Earth Surface Processes and Landforms, v. 14.

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.G., and Riggs, H.C., eds., Surface water hydrology: Geological Society of America, The Geology of North America, v. 0-1, Ch. 11.

Meade, R.H., Weibezahn, F.H., Lewis, W.M., Jr., and Perez Hernandez, David, in press, Suspended-sediment budget for the Orinoco River, in Alvarez, H., Weibezahn, F.H., and Lewis, W.M., Jr., eds., Ecosistema Orinoco: Caracas, Editorial Arts.

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 can change, meander bends can shift laterally and downstreamward, the sizes of the bed particles can change, instream bars can grow and migrate, and the amount and type of vegetation along the river can 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: Concurrent bedload and suspended-load measurements at cross sections on 93 streams in the Western United States permit analyses of the proportion of bedload to total sediment load. Bedload was measured with the Helley-Smith sampler and was composited for the entire channel cross section. The instantaneous bedload proportion at a stream cross section was found to be characterized chiefly by variability. The variability occurs in patterns or absolute magnitudes with (a) time, such as during a single hydrologic event or a runoff season, and (b) water discharge during a hydrologic event, runoff season, or longer period. The bedload proportion as a function of water discharge for a hydrograph rise and fall can show hysteresis loops and other patterns that are often associated with suspended load. For runoff seasons and longer periods, the bedload proportion can increase, decrease, have no relation, or remain reasonably constant with water discharge. The variability of the bedload proportion indicates that a cross section for the streams of this study cannot adequately be characterized by a single, representative, instantaneous bedload proportion.

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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 information is available regarding the hydraulics and mechanics of bedload transport. As scientific knowledge of river behavior advances, and is applied to management of the nation's rivers, additional understanding of bedload-transport processes will be necessary.

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

APPROACH: (1) Use continuous sampling of bedload (for example, conveyor-belt bedload trap on the East Fork River near Pinedale, Wyo.) as a control to evaluate spatial and temporal variability factors in bedload transport and to evaluate general relations between sediment movement and river hydraulics. (2) Fieldcalibrate the sediment-sampling efficiency of the Helley-Smith bedload sampler simultaneously with operation of the bedload trap. (3) Use the calibrated Helley-Smith sampler and the concurrent measurements of streamflow hydraulics in the systematic collection of bedload samples from a variety of sand- and gravel-bed streams, and within the laws of general physics, stochastically develop empirical relations of bedload transport and interpret the physical significance of the developed relations. (4) At the conveyor-belt bedload-trap research facility Initiate a tracer study using fluorescent particles (sand to fine gravel) to evaluate (a) residence time of sediment (b) average speed of varioussizes of particles (c) depth of bed material involved in transport (d) dispersion of bed material (e) short-term channel changes accompanying sediment transport (f) influence of availability of sediment on transport rate and (g) other related aspects of sediment transport. (5) Extend the fluorescent-tracer study to larger particles (coarse gravel to cobbles) by implanting microradio transmitters in individual rocks and, by periodic and (or) continuous detection by receivers/data loggers,provide time-sequence data on motion and location of separately identifiable particles. (6) Establish field sites for bedload sampling that document varying characteristics of geographic coverage (factors of hydrology, meteorology, soils, biology, and so forth); maintain one or more bedload stations as long-term observation sites so that time-trend data can be evaluated. (7) Initiate and participate, as needed, in studies comparing sampler types, sampling procedures, and analytical techniques to formulate and modify guidelines on equipment needs and field/laboratory practices; provide emphasis on relevancy to WRD mission and on need for consistency of data collection. (8) In conjunction with biologists, chemists, and other scientists, develop a field-oriented strategy for comprehensive environmental assessments; apply developed strategy to specific sites to demonstrate and document sediment-related varables as important ecological factors.

PROGRESS: (1) Field work at the bedload trap and for the fluorescent-tracer study is complete; additional dispersion analysis of fluorescent tracer was begun at University of California, Berkeley, during FY88. Bedload-transport rates, measured synoptically, vary along a river reach; bedload tonnage, measured seasonally, is nearly constant throughout the reach. Mean bedload-transport rates relate to streampower (about the 1.6 power of streampower (slope-discharge product) in excess of streampower at initiation of motion), mean bedload-particle speeds are slow (about 0.1 percent of water speed), and lengths of particle movement may be seasonally limited (distances of about 50 channel widths). (2) Radio transmitters were implanted in cobble-size rocks and movements tracked as part of bedload studies on Toklat River, Alaska (in cooperation with Alaska District, USGS, Denali National Park, National Pak Service, and Cold Regions Research and Environmental Laboratory, U.S. Army Corps of Engineers). Bedload-transport rates relate about to the 1.6 power of discharge (slope is about constant) in excess of discharge at initiation of motion and particle size (mean, modal, and maximum) increased as transport rate increased. Large moving particles (about fist size) travelled about the same distance as smaller particles (about golf-ball size). Particle speeds and distances travelled are in general agreement with observations from East Fork River, Wyo. (3) Six field sites, chosen in FY87 to help provide geographic coverage of total-load measurements, were sampled for bedload during FY88 but were discontinued thereafter. Discontinuance effectively eliminated WRD's establishment of a small hydrologic network for the routine collection of bedload data at operational field sites. During much of the FY 87-88 sampling period, flows were low in some drought-stricken areas, but runoff was normal for many snowmelt streams of the Rocky Mountain area. Most data analysis is pending; for Little Coal River, West Virginia, preliminary data analysis (in cooperation with Marshall University, Huntington) indicates that bedload may be as great as one-third of total sediment load (a greater part of total load than might be expected for streams of that region). (4) Long-term data collection continued for the eighth year at Little Granite Creek, Wyo. (in cooperation with Idaho District, USGS). Although measured total-sediment loads now constitute the longest data set available at a continuous-record gage, the period of record is still too short to allow forecasting of time trends. Generally, during the period of observation, water runoff has decreased and sediment yields have lessened more dramatically. These facts may be related to short-term weather variability rather than to long-term climate change. Values for April are in contrast to values for other months and tend to show an increase in runoff and sediment yield with time; regardless of cause, for this snowmelt stream, there appears to be a tendency for earlier runoff that indicates earlier springtime weather. (5) Comparisons of equipment and procedures were continued in collaboration with personnel in other countries (People's Republic of China) and from other USGS offices (Washington, Alaska, and Iowa Districts). Comparison of analytical procedures for concentration and particle size of suspended-sediment samples yielded nearly identical results among differing techniques of several laboratories in the United States and China. Comparison of bedload samplers were conducted at streams in Wyoming and Alaska; preliminary results between wide- (standard) and narrow-flare angled Helley-Smith type samplers indicate that endorsement of one sampler type over the other is premature (for some samples and/or for some streams, the larger samples were collected variably and alternately between the two samplers, probably reflecting hydraulic conditions, bedforms, and sediment-sorting characteristics). Comparison of bedload-sampling procedures were conducted at streams in Wyoming and Colorado. Although spatial and temporal factors must be considered, initial results indicate that, for a constant number of total samples (about 40), as the number of cross-channel locations are reduced, the mean bedload-transport rate is likely to change from an estimated true value and the value of the standard deviation of the mean rate increases. (6) Interpretation of bedload in the Wind River, Wyoming, was completed (in cooperation with the Wyoming District, USGS, and the Wyoming Highway Department). It is unlikely that either the transport rate (replenishment) or particle size (construction needs) is conducive to large-scale economic operation of gravel mining of bedload at that field site. (7) In collaboration with other USGS scientists and academic personnel (Murray State University and University of Maryland), environmental assessments were conducted on several streams in Yellowstone National Park, Wyoming. A field procedure was developed combining geomorphic aspects (river hydraulics, sediment characteristics, topography), water chemistry (pH, specific conductance, trace elements, organic carbon), and biological factors (benthic drift, invertebrates, fish). Though many laboratory analyses are pending, the procedure appears adequate for descriptive and interpretive purposes. (8) Initial comparison of measured data and numerical simulation is underway; all analyse are in progress.

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

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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 could 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 these sediments also 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 concentrations 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, ^{14}C pollen concentrations and distributions). Estimate sediment contributions from the shoreline source by use of a combination of field mapping, monitoring, and sampling at selected sites, and by laboratory measurements from available aerial 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 reaches of the Potomac .

PROGRESS: Deposition of fine-grained sediments during the 1988-water-year high flow from the Ohio River to the Mississippi River was extremely rapid in many overbank environments in the Mississippi River study reach near Hickman, Ky. More than 15 centimeters of sediment was deposited over a large area of recently logged lowlands adjacent to the main channel, and a layer of oxidized sediment 4 centimeters thick was observed in a nearby channel where only reduced sediments were present before the high water. Flooded farmlands between the mainline levees showed both deposition and erosion, and newly constructed revetments also showed variable sedimentation conditions. Sedimentation in most environments appeared to be related to geomorphology, to vegetation (presence or absence), and to approach angle for flood waters. Trace-metal and lead-210 data for four 1-meter-long cores from a Mississippi River channel abandoned about 1950 failed to reveal profiles that could be interpreted in terms of sedimentation rate, but textural data indicate deposition of about 1 meter of fine sediments in the 38 years since the channel was abandoned.

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CR273 RIVER MECHANICS

TITLE: River Mechanics

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 remains relatively constant over a period of years , 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 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 after 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 channels affected by land uses such as surface mines, reservoirs, and urbanization, the adjustment period may, in fact, be longer than the duration of change in the watershed . In watersheds where various land-use changes occur every few years, the river channel may be continually adjusting to a changing 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 can result from significant river-channel changes. One of the most frequent and important adverse effects is damage to the aquatic ecosystem. Aquatic organisms depend upon 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 impacts 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 impact of channel change upon engineering works or navigation. On the other hand, certain aspects of river-channel changes are of greater importance to the aquatic ecosystem than to 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 in response 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 controlling these characteristics of river channels as well as the rate at which they function. Formulate mathematical models of the processes as required for longitudinal routing of water and sediment. Develop new analytical tools for describing river-channel adjustment.

APPROACH: Study, in detail, the movement of bed material through a reach of channel considering the transport of bed material, distance transported, and location (bed, banks, or bar) of deposition for each size fraction. From measured bedload and suspended-transport rates, detailed measurements of flow structure, and mapping of channel features, describe the movement of bed material through the study reaches. To the extent possible, generalize these observations to formulate a physically correct model of sediment movement by size fraction. In addition, reconstruct the sequence and rate of adjustment for historical examples of river-channel change, to provide the temporal context in which to view the hydraulic characteristic at a particular point in time.

PROGRESS: During the 1989 fiscal year, three laboratory flume studies were conducted with a laser-Doppler velocimeter. In the first study, a comprehensive data set describing the velocity and Reynolds stress fields over two-dimensional bedforms was obtained; the mesurements are being used to improve computational models for flow over bedforms. In the second study, measurements of velocity and Reynold stress over beds composed of well- and poorly sorted material were collected to assess bed roughness. Sections of the flume bed were preserved, and current work is focused on the development of stereophotographic techniques for determination of bed roughness. Reduction of the flume data indicates that naturally emplaced beds may have roughness values significantly higher than those computed from the results of Nikuradse, a result that has important implications in developing a physically-based understanding of natural beds. In the third study, a flume experiment was conducted on the fluid dynamics of recirculating zones associated with a rapid expansion in channel width. The purpose of this study was to obtain information to improve the understanding of the three-dimensional aspects of recirculation zones in rivers, including the processes by which sediment enters and leaves the recirculation zones. In addition to these flume studies, an investigation of the adjustment of channel topography (including large mid-channel bars in the Green River, Utah) to variations in discharge was completed. Two-dimensional velocity fields, sediment-transport rates, and temporal evolution of channel topography at various discharges predicted by use of a fully nonlinear numerical model are in good agreement with measured characteristics of the study reach.

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

APPROACH: Make two to three boat trips per year, beginning above St. Louis and ending at New Orleans, to sample 15 to 20 cross sections of the Mississippi River and its principal tributaries. Sample cross sections for large volumes of suspended sediment by the equal-width-increment method and other methods. Concentrate and analyze suspended sediment 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 March and June 1989, bringing the total number of sampling cruises completed since 1987 to five. A pump-and-centrifuge procedure was refined for collecting and processing large-volume (500-Liter) discharge-weighted samples for analysis of toxic organics. Specific dissolved organic compounds are unique to individual tributaries (fire retardants in the Illinois River, for example), and can be used as tracers of the tributary inputs down the Mississippi mainstem. DDT and its metabolites are still present in river catfish despite the ban on DDT.

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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 human-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 of natural and induced sediment movement on geomorphology and botany 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 techniques 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 on the basis of factors such as land use, runoff, basin and landform morphology, and botanical indicators; (2) conduct research on the effects of sediment movement on landforms and vegetation 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 of ground-water flow 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: (1) Channel-morphology studies are continuing in the Plum Creek basin, Colorado. Detailed data are being collected on water and sediment entering and leaving a valley section severly modified by a 1965 flood. The data will be used to estimate total sediment transport through the reach, estimate the amount of and determine storage sites for fine sediment, and explain how storage of fines affects bottomland recovery and promotes growth of channel islands and channel narrowing. (2) Among the Plum Creek studies is an investigation of the processes by which fines penetrate alluvial-channel beds; penetration is dependent on sizes of fines relative to available bed-material pore sizes. Empirical indices of the potential for fine-particle penetration have been applied to various data and are reliable indicators, but such indices reveal nothing about processes. Currently, quantitative descriptions of available pore sizes in alluvial material are being emphasized. A model for calculating pore sizes from particle-size distributions has been modified from a University of California code. A mercury-injection laboratory technique that appears promising as a method to measure pore-size distributions is being tested with field samples. (3) Studies involving use of beryllium-10 to trace sediment on the Southern High Plains are providing insights into hydrologic and eolian processes. Recent data demonstrate that ground-water recharge occurs from playa lakes, that little recharge occurs elsewhere, and that much of the relatively coarse eolian sediment becomes dunes on lees of playas even though large amounts of finer sediment are removed by wind from the High Plains each year.

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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 erosion and the subsequent transport of material by rivers are mediated by a wide variety of closely linked chemical, biological, and physical processes. Moreover, in developed river systems such as those in the United States, these processes are subject to pervasive human-related perturbations. There is a need to develop through field and theoretical studies, a comprehensive and integrated description, of these processes for large river systems in a form that is useful to researchers in many disciplines.

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

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

PROGRESS: The bulk of project work pertains to the examination of sediment-water chemical interactions in river systems. The emphasis is on describing how the compositions of dissolved and solid load in the mainstem and tributaries relate to the geology and geomorphology of subbasins. Ongoing work includes (1) chemical analysis of suspended load, bed material, water, soil, and atmospheric precipitation; (2) petrological examination of sediment and soil; (3) preparation of geological, biological, and climatological descriptions of the basin; and (4) compilation of historical geochemical and hydrological data to document trends. In July 1988, fieldwork was completed for a 6-year-long study (funded by the National Science Foundation) of the Orinoco River system in Venezuela and Colombia. Work on the Mississippi River project focuses on the mineralogical composition of sediment as a function of particle size, and on data interpretation by use of techniques 3 and 4 above. Collaborative studies of the transport of sediment, nutrients, and trace metals in the New Jersey coastal waters and the Amazon River estuary is continuing. A computer package for the graphical interpretation of major- and minor-element data in rivers and soil waters is being designed and tested; objectives are to identify classes of weathering reactions and biogeochemical processes that control sample composition and to provide a framework for the examination of trace-constituent data. In April 1989, field work was completed for a study (funded by the National Aeronautics and Space Administration (NASA)) of the effect of soil and surface-water hydrologic regime on the biogeochemical processes controlling gas emissions, with a focus on methane and carbon dioxide. Study sites are in Panama at the facilities of the Smithsonian Tropical Research Institute. Surface water, soil water, stream sediment, and soil chemistry are also being studied. In January 1989, a proposal was submitted to NASA to begin a similar study in the United States.

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WR200 FLUVIAL SYSTEMS AND CLIMATE

TITLE: Response of Fluvial Systems to Climatic Variability

PROJECT NUMBER: WR 89-200

LOCATION: Topical Research

PROJECT CHIEF: Webb, Robert H.

HEADQUARTERS OFFICE: Tucson, AZ

PROBLEM: Understanding of the effects of climatic variability is important to development of water resources, mitigation of flood hazards, and interpretation of landforms. Climatic variability, which is characterized by increased variance and skew of a climatic signal, may be more important to water-resources evaluation than change in mean climatic conditions. Changes in variability of climate have greater effects on the probability of occurrence of extreme events, such as floods or droughts, than do changes in mean conditions. Understanding of climatic variability is of paramount importance towards estimation of flood frequency, sediment-transport rates, and channel change.

OBJECTIVE: (1) Define the extent of historic climatic variability in the western United States over the past century; (2) identify specific time periods of statistically stationary precipitation, discharge, flood frequency, and sediment transport; and (3) assess the net effects of climatic variability on fluvial systems.

APPROACH: Assess historic climatic variability through regionalization of temporal climatic signals including temperature and precipitation amounts and intensity. Determine proxy synthetic records such as tree-ring widths, varved oceanic sediment, and nonanthropogenic changes in vegetation. Examine general circulation of the atmosphere for long-term changes. Examine generation mechanisms for specific storm types, which include tropical cyclones and winter frontal storms, for frequency changes in time. Develop paleoflood records for rivers that are sensitive to climatic variability. Use regional flood frequency, streamflow, and precipitation models to assess effects of variability.

PROGRESS: Progress has been made in (1) identification of regional areas affected by 20th-century climatic variability and (2) development of new techniques for assessing flood frequency in these areas. The partial-duration flood series is separated by hydroclimatic storm type into several independent flood series. These flood series are evaluated by use of standard time-series analysis, and floods for periods that are stationary are fit to standard probability distributions by use of maximum-likelihood techniques. Mixed population analysis is then used to estimate flood frequency on an annual basis. Preliminary results indicate that, in the southwestern United States, flood frequency at recurrence intervals greater than 10 years is dominated by floods caused by tropical cyclones that dissipate over land. Flood frequency at shorter recurrence intervals is dominated by floods caused by local thunderstorms. These results are being extended to other regions of the continental United States.

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. Prepare additional synthetic ground waters, based on each of these solutions, 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 submicron filtration; (2) determine oxidation-state distribution of the plutonium by carrier precipitation and solvent-extraction procedures; and (3) for selected synthetic ground-water samples, repeat the above speciation procedures at various pH and redox-potential values.

PROGRESS: Recent project research has concentrated on americium. Whereas the solubility of plutonium in natural waters is strongly influenced by the redox properties of the waters, this effect is absent in the case of americium because americium exists in only one oxidation state under environmental conditions. Previous project research indicated that ionic strength could be a strong determinant of americium solubility in natural waters. Studies still underway indicate that ionic strength indeed has an influence, but the effect appears to be reduced at low pH. The tentative conclusion is that more than one process determines americium solubility; experiments in progress should help to resolve this question. Studies are also being made on the effect of the concentration of common anions (chloride, sulfate, carbonate) on americium solubility. These studies are of practical consequence to the disposal of radioactive wastes. Some disposal sites--the Radioactive Waste Management Complex (RWMC) at the Idaho National Engineering Laboratory (INEL), for example-- contain large amounts of plutonium-241. Because this isotope decays with a half-life of only 15 years to americium-241, it is the mobility of the latter that will determine the long-range migration of alpha activity from the site. Project personnel have served on two important committees: 1) The National Academy of Sciences Committee to Provide Interim Oversight to the DOE Nuclear Weapons Complex. Service on this Committee has involved two executive sessions, seven site visits, considerable time in the preparation of trip reports, and will require two writing sessions to prepare the final report. 2) Peer review committee to evaluate proposed plan for excavation of radioactive and hazardous wastes from burial trenches at the RWMC at INEL. Committee activities took 1 week.

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Nash, K.L., Cleveland, J.M., and Rees, T.F., 1988, Speciation patterns of actinides in natural waters--A laboratory investigation: Journal of Environmental Radioactivity, v. 7, p. 131-157.

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: Lakewood, CO

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

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

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

PROGRESS: The Warren-Averback x-ray diffraction method has been applied to the study of clay minerals, particularly 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 the geologic history of deposits that contain clay minerals and the interactions between water and clays. 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 than the commonly used Kubler index. Work on a nonpolluting, slow-release fertilizer continues, and the material continues to show promise. H. May, a new member on the project, has refined thermodynamic data used to model aqueous geochemistry of surface and ground waters by evaluation of available data sets and by calorimetric redetermination of the stabilities of the kaolin clay minerals (joint project with B. Hemingway, Geologic Division).

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CR283 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 effects on environmental quality.

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

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

PROGRESS: (1) A large set of experimental data on the effects of some commercial surfactants on the apparent solubility of DDT and trichlorobenzene has been obtained; these data form an important basis for assessing the magnitude of the solubility enhancement of a solute in relation to surfactant composition and aggregation. It was found that most surfactants at concentrations below the critical micelle concentration (CMC) have practically insignificant effects on the water solubility of relatively water-soluble organic compounds such as trichlorobenzene, because the partition interaction of surfactant monomers with relatively soluble solutes is weak. However, the significance of this interaction increases as the intrinsic water solubility of the solute decreases; therefore, the apparent solubility of DDT is significantly enhanced below the CMC by many surfactants, especially the nonionic, molecularly heterogeneous surfactants such as the Triton and Brij series. Above the CMC, all surfactants exhibit strong enhancement effects on solubilities of both DDT and trichlorobenzene because of the formation of pseudo-phase micelles acting as a microscopic organic phase. The nonpolar interior core of the micelle is found to be largely responsible for solute solubilitzation, and the magnitude of the micelle-water partition coefficient normalized for the nonpolar group content is about the same as the ordinary solvent (octanol)-water partition coefficient. (2) Unlike conventional surfactants, petroleum sulfonates consist of mixtures of sulfonated hydrocarbons and free-mineral oils, which form stable emulsions in water even at very low concentrations. The study now in progress shows that the effect of petroleum sulfonates on solute solubility is about 1.5 to 3 orders of magnitude greater than that of ordinary surfactants below the CMC, owing to the bulk-phase-like property of the former over a range from low to high concentrations.

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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 define reactants and products controlling the chemical composition of many natural waters. The effects of complex reactions, in addition to simple solution and hydrolysis, are reflected in relatively gross chemical change and interaction with fine-grained sediment.

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

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

PROGRESS: (1) Efforts were continued on the testing and application of the SNORM program to determination of solute origin. Substantial review and revision of joint efforts with Sandia National Lab personnel was done on the use of normative analysis and other geochemical information to delineate solute distribution and origin of brines in the saline strata of the WIPP radioactive waste site in southeastern New Mexico. Inferences from the normative approach have been contrasted and integrated with interpretation based on isotopes, statistics, mass transfer, and mineralogic distribution. Normative analysis is also being used to deduce and compare origins of saline solutes in marine clastic and related continental terrains of the intermontane western United States, west Texas, Gulf Coast, Spain, and Australia. Preliminary results from such analyses of saline waters from the Murray Basin and Yilgarn Block areas of Australia have been presented to collaborators. The technique appears to be helpful in delineating complex mixing phenomena and in solute derivation and characterization. (2) The initial replicate analyses of ultrafine clay from Madrid Basin aquifer materials obtained under a program conducted jointly with Spain have been used to guide representative profile selection for refinement of flow nets and subsequent mass transfer modeling. Physical, chemical, and isotopic data from more than 60 new well samples are being coupled with profile-specific clay analytics to determine the most likely mineral reactions affecting the overall hydrochemical mass balance. In addition, the comprehensive analytical experiment on ion exchange determination in these continental-basin sediments has been completed. Preliminary data analysis appears to indicate a tendency toward dilute strontium solutions. (3) A comprehensive review of chain-structure clay mineralogy was completed in collaboration with Professor Emilio Galan of Seville and was presented in a Mineralogical Society of America course. This study reinforced project-developed concepts on the hydrologic importance of these phases and accordingly produced refined solubility considerations for the influential hydrous magnesium silicates. The significance of these minerals to unsaturated zone-permeability is emerging from cooperative work with French colleagues comparing occurrences in the intermontane United States and the Mediterranean. (4) Geochemical, hydrologic, and petrographic data, supported by independent geomorphologic evidence, indicates that the freshwater flow system in the Edwards aquifer could have established itself in approximately 10,000 years. This is the consequence of rapid dedolomitization reactions in the mixing zone resulting from the invasion of meteoric water into brine-filled, permeable dolomitic units.

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

PROGRESS: Progress was made on several aspects of this project, such as (1) demonstrating the philosophical distinction between regional geochemical studies and site-specific geochemical studies due to differences in the role of physical and chemical heterogeneity as influenced by scale change; (2) emphasizing the philosophical and historical development of certain aspects of the science of hydrology, such as the role of microorganisms in geochemical studies and the importance of the perceived therapeutic value of mineral waters in the development of chemical hydrogeology; and (3) the synthesis of much of the Regional Aquifer-System Analysis contributions in the form of the commercially available book on the Hydrogeology of North America, published by the Geological Society of America.

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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 (deuterium, oxygen-18, and carbon-13) record of old (1,000-# to 10,000-year-old) ground waters, and of calcitic veins marking the sites of fossil (100,000-# to 1,000,000-year-old) ground-water discharge have not been used previously. 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 should also be pertinent to selection of sites for the disposal and long term-isolation of toxic wastes.

OBJECTIVE: (1) Infer paleoclimate and paleohydrology of selected regions on the basis of 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 deuterium, oxygen-18 and carbon-13, uranium and thorium content, and date by use of carbon-14, thorium-230, or uranium-234/238, as appropriate. Initial work with 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: 1) A 250,000-year Great Basin climatic record was published in Science on December 2, 1988. The conclusions in this paper--which challenged the Milankovitch Theory--generated considerable national and international attention and were written up at length in the New Scientist, Science News, Discovery, and in the Globe and Mail (Canada's National newspaper). 2) These conclusions we successfully defended through invited lectures and cross-examinations (by Professors Wally Broecker, John Imbrie, and colleagues) at Lamont College and Brown University. (3) Dating has been completed on an 16-inch core from Devils Hole. This specimen extends the oxygen-18 and carbon-13 climatic record back to 550,000 years.

REPORTS PUBLISHED:

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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 modeling 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, or 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 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 of the chemical evolution of natural waters. Develop theory and methods for determining reaction stoichiometry and rates from 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 by 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. Make extensive computer calculations, evaluate kinetic data, test thermodynamic models of aqueous solutions, and model the chemical evolution of ground water.

PROGRESS: The Floridan aquifer was extensively sampled in the vicinity of Valdosta, Ga., chemical and isotopic data were used to characterize local flow conditions in relation to substantial leakage from the nearby Withlacoochee River and to evaluate the redox reactions that occur in response to the large amounts of organic matter introduced from the river. An analytical capability was developed to determine the concentration of freon compounds in ground water at levels of parts per trillion; groundwater was sampled in the U.S. Geological Survey's Delmarva and Central Oklahoma National Water Quality Assessment (NAWQA) ground-water study sites for freon compounds to investigate potential for determining water age. The final in situ rates of calcite crystal growth in Devil's Hole, Nev. were determined and laboratory experiments were initiated to measure calcite growth rate under the physical-chemical conditions of Devil's Hole; the data are being used to test the mechanism of calcite crystal growth in the pre-sence of impurities. Thermodynamic data for the WATEQ generation of com-puter codes were evaluated, updated and summarized in a report. The KCl-KBr solid solution series was shown to behave reversibly at 25 degrees C, and new solubility data for this system were measured at 5 and 45 degrees C. Lippmann phase diagrams were constructed for the strontianite-aragonite system and used to evaluate reaction paths in the dissolution of solid solutions in nonstoichiometric aqueous solutions. A report describing the thermodynamic properties of magnesian calcites was published. Several recently completed reports provide thermodynamic description of solid solution-aqueous solution systems and the relations between the states of thermodynamic equilibrium and stoichiometric saturation. A generalized computer code for estimating the thermodynamics of solid solutions was completed. The reaction simulation code PHRQPITZ was completed and published; this code extends modeling capabilites of mineral-water reactions to brines and other highly concentrated electrolyte solutions. Work continues in developing a general mass-balance code for studying the chemical and isotopic evolution of ground water along hydrologic flow paths. Investigations of the extent and significance of solid solutions in controlling the migration of toxic metals at the Pinal Creek ground water toxics site in Globe, Ariz. were initiated.

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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) Tritium deposition: A manuscript was published in the Proceedings of the International Association of Hydrological Sciences meeting in Baltimore in May 1989 on the deposition of tritium over the continental United States. A more extensive version of this paper will appear as U.S. Geological Survey Water-Resources Investigations Report 89-4072, which details the deposition of tritium over the continental United States during the nuclear period. This report provides access to tritium input data so that researchers may interpret the results of their studies. (2) Selenium-tritium correlations: Preliminary results on the drain waters in the Imperial Valley indicate no correlation between the "age" of the water and its selenium concentration. Other factors besides the time that a water resides in a field apparently control selenium and dissolved-solids concentrations. (3) Origin of alkalinity: A manuscript for Journal of Hydrology has been completed and deals with the seasonal variation in the stable carbon isotopic composition (delta C-13) of dissolved inorganic carbon as a tracer of the sources of carbonate alkalinity in two small watersheds at Catoctin Mountain, Maryland. A strong inverse relationship between isotopic composition and alkalinity is primarily caused by the influx of biologically produced bicarbonate during the growing season. On a yearly basis, about 70 percent of the alkalinity in both streams is derived from calcite. At least 30 percent of the alkalinity is produced by strong acid attack on calcite. (4) Source of ammonium-bearing minerals: In cooperation with researchers in the Geologic Division, a manuscript for Economic Geology has been written in which the source and identification of ammonium-bearing minerals associated with hot springs gold deposits are discussed. The ammonium minerals appear to form from late-stage volatilization of organic matter. The range in nitrogen isotopic composition is 15 permil; compositions becoming more positive toward the surface as the amount of ammonium substitution decreases, probably in response to later oxidation of the minerals. (5) Watershed investigations: In cooperation with researchers at the Panola watershed, Georgia, the differences in water chemistry and water isotopes between incremental precipitation and throughfall have been monitored for 2 years. Unexpectedly, the isotopic composition of throughfall during storms is usually different from that of the rain. Frequently, the throughfall is depleted relative to the rain during the latter part of a storm. Therefore, the common assumption that the canopy has no significant effect on the isotopic composition of the recharge water is not valid everywhere. (6) Nitrogen isotope sample-preparation technique: A manuscript for Analytical Chemistry has been completed in which a new method is described for combusting organic and inorganic materials for delta N-15 determination. Addition of calcium oxide to the standard tube-combustion technique produces cleaner nitrogen gas than was previously possible; hence, isotopic analyses are more precise and accurate . The new technique requires no additional sample purification and thus is ideal for use with multiport automated systems. (7) Carbon dioxide-dinitrogen oxide separation technique: Carbon dioxide samples from unsaturated zone and atmospheric (global carbon dioxide) studies contain dinitrogen oxide that can cause erroneous oxygen and carbon isotope measurements of the carbon dioxide. A gas-chromatographic separation technique has been developed to quantitatively separate the two compounds. (8) Great Basin investigation of vein calcite: Carbon and oxygen isotope analysis of vein DH-11 from Devils Hole, Nev., confirms the hypothesis (based on data from vein DH-2) that the last interglacial began prior to 147,000 years ago, about 17,000 years earlier than indicated by the marine oxygen isotope record, and extended glacial cycles records to approximately 600,000 years ago.

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

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

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

PROGRESS: 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 borehole UZ-5 and a series of shallow (approximately 15-meter) boreholes on Yucca Mountain. 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. During the past year, about 1,000 samples have been variously analyzed for these constituents. After nearly 5 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) has 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 part permillion, with a vaguely defined increase with depth. The open borehole UZ-6S exhales approximately 10^6 cubic meters of gas during the winter months. The chemical and isotopic similarity of gases in UZ-6S and in the 15 meter boreholes strongly indicates a shallow and local origin of the UZ-6S gases. A summary of the existing theory of multicomponent gas transport indicates that Fick's Laws alone may not be adequate to describe diffusive gas fluxes in unsaturated zones.

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NR122 GROUND-WATER DISPERSION

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

PROJECT NUMBER: NR 81-122

LOCATION: Topical Research

PROJECT CHIEF: Wood, Warren W.

HEADQUARTERS OFFICE: Reston, VA

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

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

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

PROGRESS: (1) As part of a Regional Aquifer-System Analysis (RASA), Warren W. Wood and Walton Low described the solute chemistry of the Snake River aquifer system in Idaho in a U.S. Geological Survey Professional Paper. This report states that calcite and silica are precipitating in the aquifer and that olivine, pyroxene, plagoclase, and pyrite are being weathered from the geologic framework. In addition, mass-balance analyses indicate that large amounts of sodium, chloride, and sulfate are released from fluid inclusions and flushing of grain boundaries and pores of detrital marine sediments. The aquifer system was determined not to be a large mixing system that simply stores and transmits water, as had been previously assumed, but a system that is undergoing rapid diagenesis and that is both a source of and sink for solutes. (2) Matrix porosity in the grains forming the Cape Cod, Massachusetts, aquifer was described by Warren W. Wood, P.P. Hearn and T.F. Kraemer in a report for the U.S. Geological Survey Toxic Waste Program. Laboratory evaluation by means of air-abrasion mill, mercury porosimetry, scanning electron microscope, X-ray diffraction, and column and batch solute tests provides strong evidence for existence of matrix porosity and solute diffusion in the interior of grains that have undergone weathering. (3) Double Lakes, a saline lake near Tahoka, Tex., was selected by Warren W. Wood, Leonard Konikow, and Ward Sanford to test the hypothesis that hydrodynamics of fresh ground water and dense lake water can control the solute chemistry in saline lakes and the surrounding ground water. The proposed process is believed to cause chemical differentiation during evaporation and concentration of certain solutes, which may, under certain conditions, escape from what appears to be hydrologically closed basins. During initial field-work, 30 piezometers surrounding the saline lake were installed, geophysical and drillers logs were obtained, and samples for solute and isotopic analyses were collected. Core was collected to date, by uranium disequilibrium method, critical sections of the geologic framework.

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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 alter the quality of water and affect the inorganic reactions. The hydrogeologic controls on organic-inorganic reactions and the rate and progress of such reactions are not well understood. This project focuses on the occurrence and fate of organic compounds in (1) contaminated aquifers, (2) soils, and (3) lake sediments.

OBJECTIVE: Increase the understanding of reactions involving organic matter and evaluate the significance of these reactions in geochemical studies. (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 for organic-rich environments.

APPROACH: Select several organic-rich environments for which chemical and hydrologic background data are available 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 anaerobic. Determine the types 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: (1) In field and laboratory investigations on the degradation of organic compounds in contaminated aquifers, the geochemistry of ground water was shown to be significantly altered by chemical reactions. Hydrocarbons from crude oil floating at the surface of a shallow aquifer near Bemidji, Minn., are attenuated by several reactions that include iron and manganese reduction and methanogenesis. The concentrations of dissolved chemical species and delta C-13 isotopic values indicated that the anaerobic plume has become progressively more reducing over a 4-year period. The water-soluble aromatic hydrocarbons are transported downgradient and are degraded by microbial processes that produce volatile organic acids as intermediate compounds. These organic acids are related structurally to the parent hydrocarbons. Laboratory microcosm experiments confirm that certain aromatic hydrocarbons are degraded anaerobically. This is the first field evidence coupled with laboratory experiments demonstrating that these compounds are microbially degraded under anaerobic conditions. (2) The degradation of organic material in contaminated aquifers alters the geochemistry of the aquifers, and heterogeneities in the aquifer matrix become more important in transport processes. For example, the geochemical facies can change from an aerobic system with low concentrations of chemical constituents to a reducing environment with high concentrations of chemical constituents in a vertical interval of a few tens of centimeters. Downgradient flowpaths in contaminated aquifer systems can be on the order of tens to hundreds of meters and are difficult to delineate, in contrast to uncontaminated regional aquifers in which the aqueous geochemistry is vertically uniform within a lithologic unit and downgradient flowpaths are on the order of tens or hundreds of kilometers.

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

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

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

Chemistry, Geologic Division. Cooperation with Dr. Howard C. Hopps, Curators Professor of Pathology, University of Missouri Medical School, throughout this study.

PROGRESS: Results of ground-water sampling in a area affected by Balkan endemic nephropathy (BEN) in Yugoslavia have yielded some interesting results. Data on inorganic constituents, (including nitrogen species) in well water indicate that, of the constitnents determined, only silica may be of interest to medical researchers. However, data on organic constituents in well water indicate the presence of numerous coal-derived organic compounds. Many of these compounds are of interest to medical researchers. Also of great interest is the fact that almost all BEN areas correspond to drainages underlain by Pliocene brown coals. A pilot project has been started with personnel from U.S. Geological Survey, National Mapping Division, U.S. Environmental Protection Agency, and U.S. National Institute of Health - National Center for Health Statistics; to use a geographic information system (GIS) to determine relations between environmental factors and human health. The most significant finding to date is that some very large data bases from these agencies can be integrated into the GIS system. Preliminary results from sampling of shallow drinking-water wells and from discusions with local health officials on the Great Hungarian Plain indicate that, except for methemeglobinemia in infants, there appear to be no discernable human health effects from consuming drinking water with very high concentration of nitrate.

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 have 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 semiquantitatively 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, under carefully controlled conditions, to examine specific aspects of behavior. 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) Reestablished radiochemical laboratory in Reston, Va. (2) Determined solubility of radon in water of various ionic strengths at 25 degrees Celsius and checked against previous work in preparation for further work with organic liquids. (3) Established the feasibility of using Ra-228 as an indicator of water residence time in a lake or reservoir basin. Lake Cayuga in New York State was used as a test case. (4) Made progress in using uranium-thorium series radioisotopes to date formation of sediments in saline lake environments. (5) Used Na-22 to show diffusion of solute into matrix grains of the Cape Cod, Massachusetts aquifer. These grains show considerable internal porosity.

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-modeling methods may not be well adapted to the situations encountered in practice. As a result, it may be impossible to assess properly the availability of a given water resource or to predict the effects of certain human activities or management practices 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 effects of solute transport in the unsaturated zone on water resources and environment quality. Include in the study chemical reactions involving radioactive nuclides as well as reactions of certain solutes found in industrial and agricultural effluents. Develop mathematical models aimed at managing subsurface water quality.

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

PROGRESS: A study was begun to determine the processess that affect PCB release from river sediments. Columns of sediment from the Lower Fox River, Wisconsin, were eluted under a variety of conditions. Initial results verified the efficacy of the proposed experimental procedures.

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

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

APPROACH: (1) Conduct experiments in the laboratory by use of physical-chemical techniques to characterize surfaces and to measure adsorption behavior as the type of solute, type of surface, and water composition are varied; (2) use controlled laboratory solutions in both kinetic and equilibrium studies to evaluate the importance of surface reactions for a given solute in a given geochemical environment; (3)

develop quantitative phenomenological models to describe observed laboratory results and predict the behavior of solutes under other experimental conditions with the aid of a computer; and (4) conduct field studies periodically to assess the applicability of the models to natural aqueous systems.

PROGRESS: A field study of the transport of conservative and reactive solutes was begun in the shallow sand and gravel aquifer at the Ground-water Toxics site at Otis Air Force Base (Massachusetts). Reactive tracers included in the natural-gradient tracer tests were zinc (complexed with an organic ligand), hexavalent chromium, and selenium (as selenate). Three injections were performed, each characterized by differences in ground-water redox conditions. Aquifer chemistry had a major effect on the transport of Zn, Cr, and Se. Retardation of Zn occurred when it was partially displaced from the organic complex by iron and aluminum leached from mineral phases in the aquifer matrix. Chromium was attenuated in the anoxic zone, even when dissolved oxygen was introduced by injection, because of reduction to an immobile Cr(3+) species. Retardation of hexavalent chromium and selenate was observed only in oxidized recharge water, which had a lower pH and background salt concentration than did water in the anoxic zone. Selenium reduction was not observed in the anoxic tests. Modeling transport of these reactive solutes requires that changes in aqueous speciation along the flow path be considered. Ongoing studies of the surface and bulk properties of the mineral ferrihydrite and its sorption kinetics are continuing.

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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 geothermal-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 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 by means of present and currently developing computer programs.

PROGRESS: (1) A monitoring program has been established for several Cameroonian lakes to assess the possibility of another similar disaster similar to that of 1986. This has shown that recharge rates of CO_2 are slow. (2) Fluids from the newly-deepened Cajon Pass Borehole, California, were collected and analyzed for their gas, water, and isotopic compositions. The data showed isolation of fluids in proximal fracture systems, and also showed that some of the fluids recharged during Pleistocene glacial periods. (3) Several hundred waters from the Carson Basin, Nevada, and Yakima River, Washington, were analyzed for their isotopic composition. (4) Isotopic data showed that water from the Varian-Phillips well near Parkfield, Calif., is a metamorphic fluid. The discovery that this water is isolated from the meteoric cycle may explain high fluid pressure (120 atmospheres) at this site on the San Andreas Fault.

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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 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: (1) Final papers and reports from the International Stripa Project on geochemistry of ground water in granitic bedrock to depths of 1 kilometer have been reviewed and revised for Director's approval. (2) Participation has begun in the International Pocos de Caldas Project to investigate natural analogs of high-level radioactive-waste repositories. Analyses of ground water from an open-pit uranium mine have been reviewed, evaluated, and revised. Chemical modeling of these results has begun. Ground waters are enriched in potassium and show the influence of pyrite oxidation and fluorite dissolution. (3) Revised equilibrium data for water-mineral reactions in natural waters have been compiled and reviewed. These data provide some of the best available equilibrium constants for the purpose of chemical modeling in low-temperature (0-100 ^{o}C) systems. (4) A report is nearly finished on a comparison of trace-element determinations, for a wide range of concentration in acid mine waters, made by inductively-coupled plasma spectroscopy, direct-current plasma spectroscopy, graphite-furnace atomic absorption spectroscopy and UV-visible spectrophotometry. (5) Profiles of water chemistry in Mono Lake (major and trace elements, especially iron and arsenic) were obtained after the autumn 1988, turnover. This is the first turnover [event] since the onset of El Nino in 1982-83. The first paper on the redox species in Mono Lake has been prepared and reviewed. In this paper a mass balance on iron and arsenic comparing preturnover and postturnover conditions is described. (6) New data on the solid-solution solubiities, isotopic fractionation, and x-ray parameters for the potassium-sodium-hydronium jarosites have been obtained. (7) Collaboration with Doug Kent and Jim Davis on aspects of selenium geochemistry at the Otis Air Force Base, Cape Cod, Massachusetts has been initiated. Selenium analyses have been completed and interpretations are underway.

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Nordstrom, D.K., and May, H.M., 1988, Aqueous equilibrium data for mononuclear aluminum species, in Sposito, Garrison, ed., The Environmental chemistry of aluminum: Boca Raton, Fla., CRC Press. p. 29-53.

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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: Most of the project's field work was carried out in Paradox Valley, Colorado, (with the Bureau of Reclamation on the Paradox Valley Salinity Control Project). The Bureau has drilled 11 shallow ground water wells and a deep (16,000-f.t.) injection well. In order to arrest the contamination of Dolores River with about 200,000 tons per year of dissolved chemicals, the Bureau plans to pump water at a rate of about 1.5 cubic feet per second from the shallow aquifer into the injection well. The shallow water wells have been sampled; Samples from the injection aquifer also were obtained by use of douwnhole samplers. Results of project studies, supported by hydrothermal experiments by Bischoff (Geologic Division), indicate that injection of untreated shallow brines (total dissolved solids concentration of approximately 250,000 milligrams per liter) into the Leadville Limestone aquifer will result in precipitation of about 20 tons of anhydrite per day . The main part of the project's effort was completing, validating, and documenting the geochemical code SOLMINEQ.88. This code carries out speciation-saturation, mixing, and mass-transfer computations involving dissolution-precipitation, ion exchange-adsorption, boiling, and gas partitioning in water-oil-gas. The code may be used to study water-rock-gas-oil interactions at temperatures of 0 to 350 degrees celsius, pressures of 1 to 1,000 bars and salinities of 0 to 6 molal. In addition to the Water-Resources Investigations Report on SOLMINEQ.88, the project chief authored a chapter for USGS Professional Paper; five journal articles (see Bibliography), four as the senior author; and a chapter on chemical geothermometers for a special Society of Petroleum Engineers volume. He participated in six meetings, one international and five national. He acted as Guest Editor on a special volume of Geophysical Research Letters on Cajon Pass and continues as Associate Editor of Applied Geochemistry.

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Kharaka, Y.K., and Mariner, R.H., 1989, Chemical geothermometers and their application to formation waters from sedimentary basins, in Thermal history of sedimentary basins--methods and case histories: Springer-Verlag, no. 6, p. 99-117.

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 Mountain Range, where the chemical geothermometers indicate much lower temperatures of water-rock equilibrium than the sulfate-isotope geothermometer and the geologic setting seem to indicate. This discrepancy could be due to simple mixing of thermal water and freshwater or rapid equilibration of water with surrounding country rock as the fluids rise to the surface; alternatively, the sulfate-isotopic composition could be an artifact reflecting the original source.

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

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

PROGRESS: (1) Discharge rates of thermal fluids in the Cascade Range of the western United States. correlate with the type and amount of

volcanic activity in the segments that make up the Cascade Range in California, Oregon, and Washington. Heat discharged by hot springs in the respective segments of the Range correlate strongly with the volcanic rock extrusion rate (<2 millions years ago) when convective heat and rock extrusion rates are normalized per unit of arc length in that segment. Within each segment, convective heat discharge is highest near young silicic rock, although not all young silicic rock are clearly associated with hot spring systems. (2) Work began on determining the relation between Mammoth Hot Springs at the north side of Yellowstone National Park and La Duke Hot-Springs just outside the Park. The National Park Service is concerned that geothermal development at La Duke will cause irreversible changes in thermal features at Mammoth. Preliminary modeling studies indicate that La Duke water (major elements) could be related to Mammoth water by dilution and a series of geologically probable reactions. However, available data for the conservative elements chloride and bromide are very different (Br/Cl) and may indicate that the water feeding the two systems circulates through different rock types.
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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 well known and is considered to be one of the most important environmental problems. The widespread distribution of these anthropogenic substances, in addition to naturally occurring organics and their detrimental impact on the Nation's water resources, points to the need to understand how these substances act and react in the environment. Knowledge of transport, persistence, transformation, solubility, sorption, and reaction kinetics is needed to determine the fate of the substances in the hydrosphere.

OBJECTIVE: (1) Identify organic substances associated with a given field problem, in aqueous and nonaqueous 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 from 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 analyses; (2) do sorption studies by means of column technology previously developed in this laboratory; and (3) conduct work at two field sites on organic wood preservatives, which are ground-water contaminants, and initiate work at two other field sites where the ground water is contaminated by crude and refined petroleum products.

PROGRESS: The behavior of 51 solutes from creosote infiltrating the ground water at Pensacola, Fla., was investigated. The solutes and alteration products in the sand and gravel aquifer were indentified and quantified to study variations with distance and with depth relative to the source. A major part of the effort was refinement of high-performance liquid chromatography, gas chromatography, mass spectrometry, and computer data handling, for characterization and measurement of organic compounds in water and sediment. Organic compounds in samples collected in the aerobic-anaerobic transition zone were significantly different in makeup than in either the aerobic or the anaerobic zone. Characterization of alteration products isolated from laboratory anaerobic digestors identified metabolites from carbazole, indole, phenol, and polynuclear aromatic hydrocarbons. This information is being combined with chemical data from the field site to compile a complete interpretive report on the fate of the creosote compounds in the contaminated aquifer at Pensacola, Fla.

REPORTS PUBLISHED:

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Goerlitz, D.F., and Franks, B.J., 1989, Use of on-site high performance liquid chromatography to evaluate the magnitude and extent of organic contaminants in aquifers: Ground Water Monitoring Review, v. 9, no. 2, p 122-129.

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 the response of a water body to contaminants 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 mechanisms 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. Use high-sensitivity solid-state electrochemistry. Include both controlled laboratory studies and studies of natural systems. Conduct detailed field projects to quantify the significance of mineral substrates 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: (1) Work continued on an investigation of hetergeneous redox reactions on mineral surfaces involving transition metals. Aqueous chemical data coupled with solid-state electrode measurement and XPS surface analysis confirmed that ferric iron, hexavalent chromium, and pentavalent vanadium are reduced on magnetite and ilmentite surfaces. The surface reaction that controls this electron transfer involves surface dissolution of ferrous iron coupled with solid-state transition to a maghemite structure. (2) Synthesis of existing data on the role and characterization of reactive surface areas on mineral dissolution was also conducted with adddition laboratory determination of surface area effects related to climate and duration of weathering. Results indicated that natural surface areas are much larger than generally assumed based on laboratory studies and that estimates can be projected by assuming a direct relations to particle diameters. No fractal component was demonstrated. Kinetic models employing geometric-surface estimates were shown to generally overestimate reactive surface areas by 1 to 2 orders of magnitude. (3) Progress continued on characterizing Se distributions in the Central Valley of California at Kesterson and at the Coastal Range source area. Conditions controlling Se release in the latter case include deep weathering and extensive outcropping of Se-containing marine Tertiary-Createaceous sediments, a result of the inherently unstable landscape; the oxidation of disseminated pyrite, in which alkaline conditions are maintained by extensive carbonate buffering capacity; the inherent mobility of selenate, the oxidized from of Se; and, finally, the partial incorporation of Se in hydrous sulfate salts in the surface soils. In contrast, Se immobization in the shallow aquifer beneath the Kesterson Reservoir was found to be controlled by reduction reactions by microbial activity and dissolution of iron-containing minerals. (4) Work was completed on studies of the extent and rates of water-rock reaction in the Long Valley and Valles hydrothermal systems. Results demonstrated a close correction in water-rock rations based on oxygen-18 and Cl mass balances indicating that the reaction of rhyolitic glass is controlling rates of reaction. This was experimentally confirmed by release rates of Cl, B, and Li, which obeyed a generalized Arrhenius rate equation in the case of the Bandelier Tuff.

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 over lakes, which are basic controls on evaporation, have been studied in detail in for only a few large reservoirs in the Western U.S. . 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 individuals 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. Integrate chemical flux and biological studies with the hydrologic work at selected sites.

PROGRESS: (1) Continued test-drilling program at Williams Lake, Minnesota, and Mirror Lake, New Hampshire, to better define the geologic boundaries of the ground-water-flow systems associated with the lakes. Additional water-table wells were constructed at each of these sites as part of the drilling program to better define the water-table configuration in selected parts of the watersheds. Additional water-table wells were constructed at Island Lake, Nebraska, as part of cooperative studies with the U.S. Fish and Wildlife Service (USFWL) on understanding plant-water-soil relations along the wetland-to-upland transition zone at the edge of wetlands. (2) To facilitate better understanding of the dynamic changes in ground-water-flow systems at the edge of surface-water bodies, additional groups of wells were instrumented with recorders at Mirror Lake and Williams Lake. (3) Because of the greatly different water chemistry in various parts of the ground-water system and in various wetlands at Cottonwood Lake, North Dakota, three large soil pits were dug along a topographic profile to study fracture distribution and solid-phase chemistry. This work is being done in cooperation with the University of Wisconsin and USFWL. (4) Instrumentation was set up for complete energy-budget studies of Shingobee Lake, Minnesota, as part of the Interdisciplinary Research Initiative. (5) Analytical work and report writing is focused on evaporation studies of Williams Lake. Three reports are currently in progress.

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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 are needed for obtaining undisturbed and disturbed geologic samples for laboratory analyses, and for conducting isolated-zone tests by use of inflatable packers.

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 a variety of drilling conditions 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 feet) and for hydrofracting or deep testing (>1,000 feet).

APPROACH: Collect cores and samples that are adequate for laboratory analyses; evaluate and adapt existing tools and design new tools for isolated aquifer testing. Develop 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 examining mud-rotary-drilled holes in detail . Provide consulting and advisory assistance to U.S. Geological Survey field offices. Coordinate all efforts with Borehole Geophysical Research Project.

PROGRESS: Air-rotary drilling and coring has been completed for the Pierre Shale research-drilling project near Hayes, S. Dak. Two 91/2-inch-diameter observation wells (pumping-test production wells) were drilled and five other sites were cored by the wireline-rotary method on a research lake-drilling study near Tahoka, Tex. Teasdale completed a field visit to Bangladesh as drilling expert for the U.S. Geological Survey, Office of International Geology, Geologic Division. The Bangladeshis were given "hands on" field instruction on wireline-coring techniques and equipment at an exploration coal-drilling camp in northeastern Bangladesh near Khalashpur. While at the field camp, Teasdale wrote a training manual on wireline-coring practices and techniques for use by the Bangladeshi drilling trainees. Training lectures on drilling, coring, and sampling techniques were also presented to the drilling staff and the Deputy Director General of the Geological Survey of Bangladesh, who was in attendance. A complete "consultants' report" was prepared by Teasdale upon his return from the field to Dhaka and a rough draft submitted to the Director General (Bangladesh Survey), the Project Coordinator, and also, the U.S. Embassy in Dhaka.

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

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

APPROACH: Log selected drill holes, determining core analyse, 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. Modify equipment and develop log corrections on the basis of these comparisons and calculate the statistical accuracy of log data.

PROGRESS: Borehole geophysics and hydraulic tests have been used to characterize fracture permeability as part of continuing research in techniques for the selection of sites for radioactive waste storage. Extensive field testing has continued on a new heat-pulse flowmeter and a new acoustic sparker-source logging system, and several improvements were 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. A.E. Hess published a report documenting the mechanical and electrical components and fabrication of the heat-pulse flowmeter. R.H. Morin published journal articles on fracture permeability characterization by means of flowmeter logs. F.L. Paillet produced a review paper on the application of acoustic logging techniques to fracture characterization at radioactive-waste sites.

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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 are not generally available for application to general field situations where the flow system is complex and hydrologic data are inexact.

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

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

PROGRESS: (1) Parameter covariances contained in the conditional distribution of parameters, given the observed values of dependent variables, were incorporated into a general method of computing conservative, nonlinear confidence intervals on output from a ground-water-flow model. Tests of the new methods show that (a) a poor prior distribution (in which the modal set of parameters is a poor estimate of the true set) produced wider and more asymmetric confidence intervals than a good prior distribution; (b) widths of confidence intervals were sensitive to the assumed variance of the errors, so that this variance must be accurately estimated from the calibrated model; and (c) the new confidence intervals are much smaller than confidence intervals based on prior information only because of reduced parameter variances and increased parameter correlations resulting from including the observed data. The confidence intervals based on prior information only and the new confidence intervals can be effectively employed in a sequential method of model construction whereby new information is used to reduce confidence interval widths at each stage. (2) A Gauss-Newton nonlinear regression procedure was derived for estimating aquifer-system parameters such as transmissivity, hydraulic conductivity, and storage coefficient, and values at constant-head and defined-flux boundaries for confined aquifer systems simulated using the U.S. Geological Survey's three-dimensional, transient, modular, finite-difference ground-water flow model (MODFLOW). (3) A computer program was developed that solves the equations produced by MODFLOW by the the preconditioned conjugate-gradient method. Two preconditioners not previously available are included. (4) Based on the fictitious-point method, a transform-space expression of the global dispersive flux for transport in heterogeneous porous media was derived. Second and higher spatial moments for a pulse input of tracer were analyzed for highly stratified media; departures from classical Fickian behavior were noted. (5) Initial work on the paleohydrogeology project in the Amargosa Desert was performed; sites of Neogene carbonate deposits were investigated and samples were collected. This initial phase indicates a strong correlation between style of tectonic deformation and deposition of carbonates and provides evidence for a syntectonic origin.

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CR200 UNSATURATED ZONE FIELD STUDIES

TITLE: Field Applications of Unsaturated Zone Flow Theory

PROJECT NUMBER: CR 69-200

LOCATION: Various Sites-in Colorado, Kansas, Nebraska, Tesas

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 effects 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 models being developed by the project staff.

PROGRESS: (1) An eddy-correlation experiment to measure lake evaporation was completed at Island Lake, Nebraska, that indicated two surprising results--high nighttime evaporation rates and much higher water loss from an area covered by bullrushes than from open water. (2) Inexpensive measurements of temperature and vapor-pressure variance have proven useful in estimating evapotranspiration. (3) Topographically affected air-flow estimates have been refined, and the principal direction of the permeability tensor for fractured tuffs at Yucca Mountain has been identified from tracer-test results. (4) The finite-difference transport simulation aspects of the variability-saturated flow code VS2D have been documented, and a code simulating transport by the modified method of characteristics has been developed and tested. Effects of spatial variability of soil hydraulic properties on processes occurring within the unsaturated zone at the Sheffield, Ill., low-level radioactive-waste site have been analyzed and reported on. (5) Experiments to measure methane consumption from a variety of soil and climate types have been conducted and are being analyzed in terms of the global atmospheric methane budget. Experiments also are underway to determine bulk radiocarbon emanations from low-level radioactive-waste sites in Illinois and New York by analysis of tissues of trench-cap vegetation.

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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 actual and potential ground-water contamination problems. 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 to 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 was nearly completed on a two-dimensional microcomputer, interactive version of HST3D (HST2DM) with graphical input and output featurs 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 was continued on coupling HST3D with a multispecies chemical-equilibration calculation for application to nitrogen-compound transport. A foreign visiting scientist from the Technical University of Denmark spent 2 months in Denver working on this cooperative project. The best equation formulation and solution methods were determined by use of a one-dimensional model. Field data collection at Cape Cod was completed. Batch experiments are nearly completed; results show that molybdate adsorption in the aquifer should vary with changes in the local ground-water chemistry. One set of column experiments has been completed, and data show that molybdate adsorption is partially dependent on rate processes. A solute-transport model with side-pore diffusion was developed to simulate the column data. A second set of column experiments is near completion. A study of acidic ground-water contamination from copper mining at Globe, Ariz., has a goal 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 principal mechanism for this removal is related to the neutralization of hydrogen ion concentration, which leads to a precipitation of metals. The unconsolidated alluvium has the capacity to neutralize approximately 1 to 2 pore volumes of acidic water. Work is underway to simulate the observed changes in aquifer chemistry by use of the geochemical model PHREEQE. Estimates of plume breakthrough time have ranged from 1 to 15 years.

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

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

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

PROGRESS: Instrumentation in the Pierre Shale in central South Dakota has provided sufficient information on the shale hydraulics to permit a coherent interpretation of the ground-water-flow system in the shale; in many respects this culminates several years of effort directed at understanding this complex and interesting system. Specific highlights of the last year include (1) successful permanent installation of a second set of digiquartz pressure instruments 350 meters north of the first site and continued flawless performance of the first set of instruments (installed 10/87). The second set of instruments are consistent with the first in indicating, after equilibration, a strong underpressuring with the lowest heads at midlevel in the shale. They also show that horizontal hydraulic gradients are virtually absent flow is vertical. The data are retrieved in near real-time through a modem-telephone line connection. Sufficient records from both installations are now available to warrant interpretation with some confidence. (2) Development of a theoretical, physically based explanation of the long equilibration times observed for the pressures in the boreholes. Elastoplastic deformation theory is consistent with near-field dilatational effects sufficient to cause the lags seen; these could cause misinterpretation of short-term observations of the potentiometric head in other "tight" units. (3) Explanation of the observed underpressuring consistent with the region's geologic history. Recent (last million years) rates of erosion (10 to 20 centmeters 1,000 years) inferred by geologists for this area are sufficient to have generated the observed underpressures. (4) Reconciliation of results with earlier work that suggests important secondary permeability in the shale. A conceptual model incorporating sparse fractures with large intervening blocks is able to explain all observations. This conceptual model shows that flow in this classic confining layer is really quite complex, consisting of nearly steady-state regional behavior coexisting with strongly transient local flow.

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 human-induced stresses, the interaction of which determines both its preservation and its use as a multifaceted natural resource for water supply, energy production, and subsurface storage of energy and materials. Study of subsurface problems requires (1) synthesis of a theoretical framework of physics of single-phase and multiphase fluid flow, mass and energy transport, and fluid-phase change as applied to the subsurface environment, and (2) describing subsurface behavior on the basis of 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-phase and multiphase fluid flow, mass and energy transport, and fluid-phase change. Apply these methods to field problems to illuminate hydrological relations that are important in both the preservation and optimal use of the subsurface.

APPROACH: Measure subsurface flow and transport in the field to develop mathematical descriptions of the system. Study system behavior by use of analytical and (or) numerical solutions of the mathematical description, based on either hypothetical or field problems. Develop simulation models and analytical methods for quantitative analysis of subsurface problems, as well as novel measurment techniques, as byproducts of the investigations.

PROGRESS: Methods for parameter estimation and model discrimination in one-dimensional solute transport have been developed. Optimal network-design strategy has been successfully tested on the field-scale tracer test at Otis Air Force Base, Cape Cod, Massachusetts, and has demonstrated the value of employing simple models of transport on sparse data sets. Variable-density flow and solute-transport analysis applied to the major coastal aquifer in Oahu, Hawaii, has allowed prediction of water-quality effects of by seawater intrusion for the next 100 years under various recharge-pumping scenarios. Analysis of field measurements in Oahu, Hawaii, to determine scale effects in hydraulic and transport behavior of structured heterogeneous aquifers is underway.

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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. Contaminants have been and will continue to be accidentally and deliberately introduced into ground-water systems. Some of these contaminants are very hazardous. Because of the immediacy of such contamination problems, understanding of the physical and chemical processes needs to be increased rapidly, and mathematical models derived from this understanding need to be 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. 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: Progress was made in several areas related to solute-transport studies: (1) Several test wells were drilled around a saline lake in West Texas. Preliminary results indicate that dissolved salts are escaping from the closed basin into the regional aquifer system through a combination of density effects and diffusive transport. (2) Preliminary field studies and modeling indicate that acid springs and streams (pH <2.5) on the flanks of Poas Volcano, Costa Rica, are fed by subsurface flow from the active crater, which contains a hot, acidic (pH <0.0), brine lake several kilometers from the springs. (3) The method-of-characteristics solute-transport model has been updated to include nonlinear reaction terms. (4) A theoretical analysis of dispersion in transient ground-water flow fields has yielded apparent dispersivity relations that depend on the angle of deviation during transient flow and the ratio of longitudinal to transverse dispersivity. Flow-field transients can cause significant spreading in a direction perpendicular to the mean flow direction, this spreading could lead to erroneous calibrated values of transverse dispersivity. The analytical approach is being applied to the plume at the INEL site, Idaho. (5) The effects of changing fluid storage on solute transport in transient flow have been quantified by use of analytical and numerical models. Several published models contain erroneous approximations, although inclusion of the exact form requires only miminal additional computation. (6) Analysis of flow and transport through low-permeability confining layers indicates that diffusive transport could be very significant over geologic time scales and that diffusion could modify the concentration distribution to such an extent that the flow field is modified because of consequent changes in the fluid-density distribution. Because of the interrelation between flow and concentration, a simple analytical solution to the diffusion equation is inadequate, and a general variable-density flow and transport model is required.

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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 by use of 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 by use of 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 of existing techniques and instrumentation and quantitatively ascertaining limitations of methods. Complete comprehensive literature survey.

PROGRESS: Water-quality data have been compiled into a data set, and summary statistics for key chemical variables have been studied. The results are presently in review. Multivariate statistical methods are being used in a variety of modes to assess the chemical character of ground waters in aquifers of the Delmarva Peninsula. Cluster analysis and other multivariate methods are key methods in understanding ground-water quality in the study area.

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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 of fractured formations and their various uses, including proposed repositories for radioactive waste, a need exists to describe and better understand the physics of fluid movement, deformation, contaminant migration, and energy transport under the broad range of physical situations where fractured formations exist.

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

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

PROGRESS: Field testing of a fractured dolomite beneath a low-level radioactive-waste disposal site was continued. The site is located southwest of Chicago, Ill., and the work is being conducted in cooperation with the U.S. Geological Survey, Illinois District Office and the Branch of Nuclear Waste Hydrology (WRD). Tracer tests were conducted in a discrete subhorizontal fracture that is hydraulically continuous between several boreholes separated by more than 200 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 random field. In a related area, research on a stochastic description of contaminant movement in heterogeneous porous media also was continued. A mathematical model was developed that describes the arrival time of reactive solutes at fixed locations by use of the three-dimensional stochastic properties of the porous medium properties. The results are of importance in aiding regulatory decisions that concern solute migration in the subsurface.

REPORTS PUBLISHED:

Shapiro, A.M., and Cvetkovic, V.D., 1988, Stochastic analysis of solute arrival time in heterogenous porous media: Water Resources Research, v. 24, p. 1711-1718.

Shapiro, A.M., and Nicholas, J.R., 1989, Assessing the validity of the channel model of fracture aperture under field conditions: Water Resources Research, v. 25, p. 817-828.

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. Predict the effects of chemical and physical stresses on the quality of ground water.

APPROACH: Solve the mass-transport equation through numerical means by use of 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. Take a systems-oriented 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.

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 significantly influenced by water flow through the unsaturated zone. For many situations of hydrologic interest, inadequate knowledge prevents these influences from being properly taken into account in water-resources analyses.

OBJECTIVE: Test present theories of water flow through 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 flow 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: Continued (and completed) the first stage of adapting, developing, and testing a promising sequential (two-or-three-step) method for deriving operational transport equations. The method, now called the feed-forward (FF) method, provides increased efficiency by adapting its formulations to the fundamental features of transport-influencing reaction networks. This stage of the study considers a large variety of equilibrium-controlled reaction networks consisting of segments that contain only three or, in the case of exchange reactions, four participants. Emphasis was placed on networks containing segments of more than one reaction class. Homogeneous, classical-heterogeneous and surface-reaction classes were studied, with any number of segments per reaction class. The FF method was found to be applicable to all the cases tested. A systematic, stepwise approach to method development was employed, which revealed for certain networks and subnetworks an a priori inadmissibility, and--for some other subnetworks--irrelevance to transport dynamics. It also demonstrated that when certain subnetworks belonging to different network classes form a single network, synergism (or its reverse--antagonism) occasionally can arise and decrease (or increase) the difficulty of solving the transport problem.

REPORTS PUBLISHED:

Stonestrom, D. A., and Rubin J., 1989, Water content dependence of trapped air in two soils: Water Resources Research, v. 25, n. 9, p. 1947-1958.

Stonestrom, D. A., and Rubin J., 1989, Air permeability and trapped-air content in two soils: Water Resources Research, v. 25, no. 9, p. 1959-1969.

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

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

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

PROGRESS: Hydrologic monitoring program at Long Valley and Lassen Park were continued. Papers describing results and interpretations from these monitoring programs were prepared for colleague review. Studies of the effects of geothermal development on hot springs were initiated at Yellowstone National Park and Steamboat Springs, Nev.

REPORTS PUBLISHED:

Ingebritsen, S.E., and Sorey, M.L., 1988, Vapor-dominated zones within hydrothermal convection systems--evolution and natural state: Journal of Geophysical Research, v. 93, no. B11, p. 13635-13655.

Farrar, C.D., Sorey, M.L., Rojstaczer, S.A., Steinemann, A.C., and Clark, M.D., 1989 Hydrologic and geochemical monitoring in Long Valley caldera, Mono County, California, 1986: U.S. Geological Survey Water-Resources Investigations Report 89-4033, 100 p.

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 geothermal investigators in the Water Resources Division.

APPROACH: Plan, arrange for staffing, approve budgets, maintain technical surveillance, and advise Chief Hydrologist through appropriate staff on the progress of the geothermal program. Review needs for test drilling and other logistical support as work progresses and make neccessary funds available.

PROGRESS: Geothermal research in WRD was coordinated with that of the Geologic Division in the U.S. Geological Survey and with that of other Federal agencies. WRD 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 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 from 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 Cascades Mountain Range in Oregon and California ; (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) Select specific areas to be studied In collaboration with geologists, geochemists, and geophysicists making concurrent studies; (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. Improve existing methods 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.

PROGRESS: An ongoing study of the north-central Oregon Cascades (approximately 44'00" to 45'15"N lat.) has involved evaluation of about 250 temperature profiles and water samples from about 770 sites. In north-central Oregon, a large area of near-zero near-surface conductive heat flow occurs in young volcanic rocks of the Cascade Range. Advective heat flow measurements and a heat-budget analysis indicate that ground-water circulation sweeps sufficient heat out of areas where rocks younger than 6 Ma (million years ago) are exposed to account for the anomalously high advective and conductive heat discharge measured in older rocks at lower elevations. Earlier investigators have proposed that an extensive midcrustal magmatic heat source is responsible for this anomalously high heat flow. Instead, high heat flow in the older rocks could be a relatively shallow phenomenon caused by regional ground-water flow. Any deeper anomaly could be relatively narrow, spatially variable, and essentially confined to the Quaternary (less than 2 Ma) arc. Magmatic intrusion at a rate of 9 to 33 cubic kilometers per kilometer of arc length per million years can account for the total heat flow anomaly. Deep drilling in the areas of high heat-flow in the older rocks could indicate which model is more appropriate for the near-surface heat-flow data. The resource implications of the "lateral flow" model relative to the midcrustal heat source model are mixed. The "lateral flow" model implies a more limited resource base, but a better defined exploration target--a narrower, spottier deep heat-flow anomaly and heated ground water circulating away from that anomaly.

REPORTS PUBLISHED:

Sammel, E.A., Ingebritsen, S.E., and Mariner, R.H., 1988, The hydrothermal system at Newberry Volcano, Oregon: Journal of Geophysical Research, v. 93, p. 10149-10162.

Ingebritsen, S.E., and Sorey, M.L., 1988, Vapor-dominated zones within hydrothermal systems: Journal of Geophysical Research, v. 93, p. 13635-13655.

Ingebritsen, S.E., Mariner, R.H., Cassidy, D.E., Shepherd, L.D., Presser, T.S., Pringle, M.K.W., and White, L.D., 1988, Heat-flow and water-chemistry data from the Cascade Range and adjacent areas in north-central Oregon: U.S. Geological Survey Open-File Report 88-702, 205 p.

Ingebritsen, S.E., Sherrod, D.R., and Mariner, R.H., 1989, Heat flow and hydrothermal circulation in the Cascade Range, north-central Oregon: Science, v. 243, p. 1458-1462.

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 application to problems in the field.

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 from laboratory results. Use field data for case studies.

PROGRESS: A paper was written and approved for publication in the Proceedings of the International Conference on Fluid Flow in Fractured Rocks, Atlanta, Ga., May 16-18, 1988. This paper concerns the response of partially penetrating wells to pumping from double-porosity aquifers or geothermal reservoirs. The model was extended to include effects of a free surface. Another paper was published in Water Resources Research on the dispersion of a tracer in a radially convergent fluid-flow field. The paper describes a method for the evaluation of aquifer porosity and dispersivity from tracer-breakthrough data obtained from a pumped well. The model was recently extended to allow for tracer diffusion in the blocks of a densely fractured porous rock or in the grains of a sand aquifer.

REPORTS PUBLISHED:

Moench, A.F., 1989, Convergent radial dispersion--a Laplace transform solution for aquifer tracer testing: Water Resources Research, v. 25, no. 3, p. 439-447.

Moench, A.F., in press, The response of partially penetrating wells to pumpage from double-porosity aquifers, in International Conference on Fluid flow in Fractured Rocks, Atlanta, Ga., May 16-18, 1988, Proceedings.

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

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

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

PROGRESS: All of this project's manpower (Getzen 100 percent; Slack 60 percent) 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, Nevada, 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.

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

OBJECTIVE: To use water wells as indicators of crustal strain

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

PROGESSS: As part of the Parkfield prediction experiment a total of 17 water levels at 13 locations are being monitored. At four locations, water levels are measured in a deep and a shallow zone. Parkfield is an especially interesting site because an earthquake of magnitude 6 is predicted to occur there in the next several years. During the past year, a number of creep events were registered by water wells and nearby creepmeters. The events are of interest because they demonstrate the coherence of the data between the two types of measurement devices.

A deep well with high pore fluid pressure, approximately 1,700 pounds per square inch at the land surface, was instrumented during the year. This well approximately 5,000 feet deep and is less than 1 mile from the San Andreas Fault in the expected epicentral area of the anticipated earthquake. High- and low-frequency pore-pressure data are being collected on this well. This well should provide a wealth of pore pressure information during the actual earthquake, and this information could lead to new insights regarding the mechanism of failure.

REPORTS PUBLISHED:

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.

Bredehoeft, J. D., 1988, Will repositories be dry?: EOS, Transactions of the American Geophysical Union, v. 69, no. 9, p. 121, 131.

Belitz, K., and Bredehoeft, J.D., 1988, Hydrodynamics of Denver Basin--explanation of subnormal fluid pressures: American Association of Petroleum Geologists Bulletin, v. 72, no. 11, p. 1334-1359.

Rojstaczer, S.A., and Bredehoeft, J.D., 1988, Ground water and fault strength, in Back, W., Rosenshein, J.S., and Seaber, P.R., eds., Hydrogeology: Boulder, Colo., Geological Society of America, The Geology of North America, v. 0-2, p. 447-460.

Avon, L., and Bredehoeft, J.D., 1989, An analysis of trichloroethylene movement in groundwater at Castle Air Force Base, California: Journal of Hydrology, v. 110, p. 23-50.

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 models (hydraulic, solute, transport and thermal transport) are often used to explore aquifer-management options. Generally, models are executed repeatedly under different management scenarios and the results are compared. Use of 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 through 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: Progress was made in three diverse areas of aquifer modeling. First, work on effective model parameter values for ground water studies was completed. It demonstrated that the average zonal values in a ground-water model are not constant properties of the media, but are influenced by the degree of pumping in the basin. This result calls into question the use of calibrated simulation models for prediction if the pumping regime changes. Second, a new method was developed to analyze the influence of heterogeneity in hydraulic conductivities on remediation of contaminated aquifers. This method involves a combination of geostatistics, aquifer simulation, and optimization. It is useful in isolating the tradeoff between cost and risk in design studies for aquifer remediation. Finally, a major study of the influence of a water market on an agricultural economy was undertaken. The Arkansas Valley in southeastern Colorado was studied, and a simulation-management model was developed to target the influence of water trades among farmers on the local agricultural economy.

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 of the fluid in its liquid and vapor state with the granular materials must be understood. The effects of phase change and two-phase flow on transport processes also are important. The interactions are documented to some degree for low-temperature, low-pressure fluid. However, documentation for high temperatures and high pressures is needed for geothermal applications and at high temperatures for nuclear-waste applications. Very little information of this kind 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 general and realistic model of fluid movement and mass and energy transport in porous media. Evaluate experimentally 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. Do 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 on water transport and head . Apply fundamental laws of physics to develop equations, and solve the equations by standard numerical and analytical means. Perform limited field experiments to test the applicability of methodology developed in theoretical and laboratory studies.

PROGRESS: W.N. Herkelrath carried out laboratory and field investigations of multiphase, unsaturated, and immiscible flow in porous media. In response to requests from the Nuclear Hydrology Program and District personnel in several states, Herkelrath developed a user-friendly, time-domain reflectometry (TDR) system for measuring soil-moisture content in the field. The system was successfully used by these groups in a variety of applications. In collaboration with G.H. Leavesley (WRD, Denver), a TDR system enabling monitoring of soil moisture beneath a snow pack was developed and installed at Rabbit Ears Pass, Colorado. Soil-moisture content was measured at 12 locations every 15 minutes throughout the snowmelt period. It is expected that the data can be coupled with a suite of other measurements at the site to improve predictive snowmelt-runoff models. A program of laboratory investigations of the flow of nonpolar fluids (for example, gasoline) in porous media was begun. In collaboration with H.I. Essaid (WRD, Menlo Park), a new laboratory method was designed for determining the characteristic functions needed in modeling three-phase immiscible flow in porous media. Preliminary tests of the method were carried out in two-phase, immiscible flow experiments in a one-dimensional soil column. The technique requires rapid determination of fluid-saturation and capillary-pressure distributions in the soil. To meet this need, a miniaturized TDR probe controlled by a high-speed computerized data-acquisition system was developed and used in the experiments to measure water content. Also, a low-cost, computer-driven tensiometer/pressure-transducer system was developed to continuously monitor the capillary-pressure distribution at many points in the column. Soil cores were also obtained from the WRD oil-spill site near Bemidji, Minn. Laboratory methods were designed to determine three-phase flow parameters for these intact cores. As a first step, equipment for determining capillary pressure curves for the cores was developed and tested. The core data should provide parameters useful in modeling oil and water movement at the Bemidji spill site.

REPORTS PUBLISHED:

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

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

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

PROGRESS: Continued (and completed) the first stage of adapting, developing and testing a promising sequential (two-or-three-step) method for deriving operational transport equations. The method, now called the feed-forward (FF) method, provides increased efficiency by adapting its formulations to the fundamental features of transport-influencing reaction networks. This stage of the study considers a large variety of equilibrium-controlled reaction networks consisting of segments that contain only three or, in the case of exchange reactions, four participants. Emphasis was placed on networks containing segments of more than one reaction class. Homogeneous, classical-heterogeneous and surface-reaction classes were studied, with any number of segments per reaction class. The FF method was found to be applicable to all the cases tested. A systematic, stepwise approach to method development was employed, which revealed for certain networks and subnetworks an a priori inadmissibility, and--for some other subnetworks--irrelevance to transport dynamics. It also demonstrated that when certain subnetworks belonging to different network classes form a single network, synergism (or its reverse--antagonism) occasionally can arise and decrease (or increase) the difficulty of solving the transport problem.

REPORTS PUBLISHED:

Bahr, J.M., 1990, Kinetically influenced terms for solute transport affected by heterogeneous classical reactions: Water Resources Research, v. 26, no. 1, p. 21-34..

Rubin, J. M., 1990, Solute transport with multi-segment, equilibrium-controlled reactions--a feed-forward simulation method: Water Resources Research, v. 26, no. 9, p. 2029-2055.

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 for assessment of the suitability of underground hazardous-waste storage sites, as well as for prediction of waste movement 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 be applicable 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 on the basis of geologic and geophysical information. Investigate the effects of scale by computer simulation and stochastic and geostatistical techniques. Predict rock characteristics on a large scale from results of field tests conducted on a small scale and compare the predicted results to actual results from large-scale tests.

PROGRESS: (1) Developed method to analyze well tests in shallow bedrock aquifer overlain by regolith. Applied this method to analyze well tests [performed] at the Lee Valley site, San Diego County, California. Results provide hydraulic properties of crystalline bedrock and regolith. Wrote interpretative report. (2) Completed preliminary analysis of large-scale aquifer tests at the Waipahu site, Oahu, Hawaii. Results yield horizontal and vertical hydraulic conductivities of basalt sequences underneath the island. (3) Coorganized a field trip for the 28th International Geologic Congress (July 1989) and coauthored a field guide titled "Physical and Hydrologic-Flow Properties of Fractures."

REPORTS PUBLISHED:

Barton, C.C., and Hsieh, P.A., 1989, Physical and hydrologic-flow properties of fractures: American Geophysical Union, 28th International Geologic Congress, Field Trip Guidebook T385, p. 36.

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

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

PROGRESS: A series of laboratory experiments was done to examine the influence of temperature on infiltration at 5, 25, and 60 degrees Celsius for two soil materials, and report was prepared in which current theory for the temperature dependence of infiltration was compared to the measured results. Excellent agreement was found between theory and results for both materials. A 2-year study was completed on the feasibility of using time-domain reflectometry (TDR) to monitor tree moisture storage. The usefulness of this new application of TDR to hydrology was discussed in a recently completed report. The Department of the Interior applied for a patent on a new water purification process developed within the project. The process is discussed in detail in a recently published paper. The isothermal part of a study concerning the isothermal-isobaric water-retention characteristics of porous materials was completed for temperatures of 10, 45, and 80 degrees Celsius. Field work was completed at Hubbard Brook Experimental Forest, New Hampshire concerning the influence of geology, fracture geometry, and fracture character on hydraulic properties of ground-water/surface-water interactions.

REPORTS PUBLISHED:

Constantz, J., 1987, R.E. Moore and Yolo Light Clay, in Landa, E.R., and Ince, S., eds., History of hydrology: Washington, D.C., American Geophysical Union, History of Geophysics, v.3, p. 99-101.

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

Constantz, J., Herkelrath, W.N., and Murphy, F., 1988, Air encapsulation during infiltration: Soil Science Society of America Journal, v. 52, p. 10-16.

Constantz, J., 1989, Distillation irrigation--a low-energy process for coupling water purification and drip irrigation: Agriculture Water Management Journal, v. 15.

WR198 UNSATURATED ZONE FLOW

TITLE: Physical Characteristics that Determine Flow in the Unsaturated Zone

PROJECT NUMBER: WR 89-198

LOCATION: Topical Research

PROJECT CHIEF: Nimmo, John R.

HEADQUARTERS OFFICE: Menlo Park, CA

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

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

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

PROGRESS: (1) Computations and analysis of results from an experimental test of Richards' equation provided reasonable support, within experimental error, for the validity of generally accepted unsaturated flow theory under conditions drier than in previous tests (about 25 percent of saturation in a sandy soil). The results also support the validity of Richards' equation in a centrifugal field. (2) A new experimental technique for the measurement of saturated hydraulic conductivity (K-sat) was developed and was tested successfully by comparison to the widely used falling-head method. The new technique, which employs a centrifuge to generate large driving forces, is faster and simpler than most other methods and is advantageous for hydrologic studies involving large numbers of samples. (3) For a study of deep unsaturated-zone fluxes and aquifer recharge rates in a region of loess deposits in southeastern Washington, core samples in minimally disturbed condition were obtained from 9 to 20 meters in depth. Initial laboratory measurements of moisture properties show that these samples have distinctly atypical unsaturated characteristics in comparison to the more highly structured and sandier media that have been the usual subjects of previous unsaturated-zone moisture studies. Preliminary K-sat measurements at one site indicate maximum fluxes significantly lower than previous estimates of aquifer recharge rates by other methods.

REPORTS PUBLISHED:

Nimmo, J.R. and Akstin, K.C., 1988, Hydraulic conductivity of a saturated soil at low water content after compaction by various methods: Soil Science Society of America Journal, v. 52, p. 303-310.

WR199 FLOW OF IMMISCIBLE CONTAMINANTS

TITLE: The Fate and Transport of Immiscible Contaminants in the Subsurface

PROJECT NUMBER: WR 89-199

LOCATION: Topical Research

PROJECT CHIEF: Essaid, Hedeff I.

HEADQUARTERS OFFICE: Menlo Park, CA

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

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

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

PROGRESS: The major effort of this year has been to establish an integrated research effort coordinating the expertise of people on this project and other projects within the Survey. Because of the many complex aspects of this problem, meaningful results can only be obtained by the integration of field work, laboratory work, and numerical modeling. Capabilities are being built up in each of these areas. A numerical model to simulate three-phase flow (assuming that the air phase is at atmospheric pressure) in a vertical cross-section has been developed and verified against published experimental and numerical results. The model has been used to aid in the design of laboratory experiments for two- and three- phase flow, and it has proven to be a very useful tool in this respect. Work of a student at New Mexico Tech on flow visualization of air-oil-water systems in micromodels and residual saturations has demonstrated the complexity of the flow on the pore scale and has implications for numerical modeling at the continuum scale. Field work at the Bemidji research site has focused on characterizing the hydrology of the system, in preparation for a more detailed study of the movement of the oil lens. Other work that has been undertaken involves saltwater-intrusion problems. The multilayered freshwater-saltwater model has been tested by district personnel in New Jersey and Virginia, and this testing has resulted in improvements that have been incorporated into the model. The documentation is currently going through the Survey's review process. Simulations with the model have shown that, in many coastal aquifer systems, the position of the freshwater-saltwater interface today may not be in equilibrium with current sea level.

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. These substances are known to complex trace metals, to transport pesticides, to be precursors of carcinogenic compounds upon chlorination, and to be a food source for aquatic organisms; yet, little is known about the chemistry or source of these organic materials.

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

APPROACH: (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: Several reports are planned and in progress. Humic substances in a stream draining a bog in southern Norway were found to be strongly influenced by humic substances in soil adjacent to the bog. Other samples of humic substances in major streams and lakes in Norway were found to be much like humic substances in similar environments of the United States. Chemical analyses for hydrolyzable amino acids, pentose sugars, and hexose sugars in humic substances reveal definitive differences according to source. Analyses of humic substances for C14-age and delta C13 values also are indicators of humic sources in most cases.

REPORTS PUBLISHED:

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., 1988, Enzymatic coupling of 2,4-Dichloraphenol to stream fulvic acid in the presence of oxidoreductoses: Soil Science Society of America Journal, v. 52, p. 688-694.

MacCarthy, P., and Malcolm, R.L., 1989, On the nature of commercial humic acids, in Suffet, I.H., and MacCarthy, P., eds., Aquatic humic substances:--influences on fate and treatment of pollutants: American Chemical Society, Advances in Chemistry Series 219, p. 55-63.

Malcolm, R.L., 1989, Applications of solid state 13C-NMR spectroscopy to geochemical studies of humic substances, in Hayes, M.H.B., MacCarthy, P., Malcolm, R.L., and Swift, R.S., eds., Humic substances in soil, sediment, and water--structure of humic substances: Chitchester, England, John Wiley, chap. 12.

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

OBJECTIVE: (1) Isolate the various organic polyelectrolytes present in natural water systems; (2) determine the physical and chemical properties of the most abundant organic polyelectrolytes; (3) elucidate the mechanisms of interaction of pollutants with natural organic polyelectrolytes; (4) determine types of chemical compounds that result from the chlorination of natural polyelectrolytes; (5) characterize 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) develop nuclear magnetic resonance (NMR) spectroscopy methods for the characterization of humic materials; (7) determine and characterize organic pollutants in ground water and precipitation; (8) characterize the interaction of organic pollutants from precipitation with soil systems; (9) investigate various substrates for sample introduction;

and (10) characterize NMR spectra obtained for various compound functionalities.

APPROACH: (1) Isolate chemically unique polyelectrolyte fractions by use of column chromatography, electrophoresis, and other techniques; (2) determine the physical and chemical properties of the fractions by use of 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, by use of potentiometric titrations to measure cupric ion activity and 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; and (8) isolate organic pollutants from water systems.

PROGRESS: (1) The collaborative study with scientists from the University of the Philippines on the characterization of humic acids isolated from three different types of deposits in the Philippines has been completed. A report has been prepared and has progressed through colleague review. It is presently being revised for Director's approval. This study is part of an ongoing program on the isolation, fractionation, and characterization of humic substances from different terrestrial and aquatic environments. (2) A collaborative study has been undertaken with Dr. Josef Hejzlar of the Czechoslovak Academy of Sciences on the characterization of humic acid fractions isolated from a highly organic Czechoslovakian surface water. The C-13 NMR spectra of the fractions have been measured in our laboratory, and the spectra have been sent to Dr. Hejzlar. Some ideas on how the report on this work should be prepared, also have been conveyed to Dr. Hejzlar. (3) A study has been undertaken with a graduate student from the University of Colorado Denver Center (Ann Nefcy) to elucidate the chemical structure of a polysaccharide fraction isolated from the humic acid acid of a Philippine agricultural soil studied previously. The polysaccharide fraction has been purified by precipitation of the more phenolic components, and at the present time, methylation and hydrolysis of the polysaccharide is underway. (4) A collaborative study on the identification of polyethoxylate detergent components in natural waters has been undertaken with Jerry Leenheer's project. NMR evidence for the presence of polyethoxylate groups has been obtained from samples collected from Clear Creek in Colorado and from the Mississippi River. A report has been prepared and is presently being revised after journal review. (5) The trimethylsilyl ethers and esters of several different humic substances have been prepared. The C-13 and Si-29 spectra of these derivatives have been measured, and the concentrations of hydroxyl and carbonyl groups have been determined from the spectra of the derivations. Several different NMR pulse sequences, including one that yields a spin echo, have been used in this study. (6) A method has been developed for the isolation of hydrophilic organic acids from aquatic environments by sorption on nonionic, macroreticular resin columns. This method was developed in conjunction with Diane McKnight and E.M. Thurman. A report of the work has been written, and it is currently being revised after colleague review. (7) Three fractions of nonvolatile organic acids resulting from the biodegradation of crude oil have been isolated from a well downgradient of the point of crude oil contamination at the Bemidji, Minn. site. The organic acids and the undegraded whole crude oil have been characterized by C-13 NMR spectroscopy. The NMR spectra allow one to distinguish between the naturally occurring background dissolved organic carbon (DOC) and the nonvolatile organic acids resulting from the biodegradation of the crude oil. A report is being prepared on this work. (8) The insensitive nuclei enhanced by polarization transfer (INEPT) NMR pulse sequence has been used to study the hydroxylamine and silyl derivatives of the Suwannee River fulvic acid. Nitrogen-15 and Si-29 NMR of these derivatives allowed us to identify oximes, nitriles, hydroxamic acids, secondary amides, lactams, and the silyl esters of carboxylic acids, and the silyl ethers of phenols and alcohols. Our results show that the INEPT sequence provides quantitative Si-29 NMR spectra in much less time than does the standard inverse gated decoupled sequence. This work was done in collaboration with scientists at the University of Arizona, California State University, and the Colorado School of Mines. (9) Standard and reference humic substance samples from the International Humic Substances Society have been characterized by solution-state H-1 and C-13 NMR spectroscopy. The NMR measurements included spin lattice relaxation times, nuclear Overhauser enhancement factors, and quantitative carbon distributions. The attached proton test (APT) was used to distinguish between methyl, methylene and methine carbons. A report of this work has been prepared and has received Director's approval. (10) A second year of sampling has been completed on Lake Fryxell in the Dry Valleys of Antarctica. Organic compounds from the lake water were isolated by resin adsorption. The isolates have been freeze dried and brought back to Denver. The Lake Fryxell study is a joint effort of several WRD projects.

REPORTS PUBLISHED:

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Wershaw, R.L., Thorn, K.A., and Pinckney, D.J., 1988, Characterization of humic acid fractions by C-13 nuclear magnetic resonance spectroscopy: Environmental Technology Letters, v. 9, p. 53-62.

McKnight, D.M., Thorn, K.A., Wershaw, R.L., Bracewell, J.M., and Robertson, G.W., 1988, Rapid changes in dissolved humic substances in Spirit Lake and South Fork Castle Lake, Washington: Limnology and Oceanography, v. 33, p. 1527-1541

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Wershaw, R.L., in press, Sorptive interactions of humic substances: Environmental Health Perspectives (EHP), v. 83.

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Aiken, G.R., and Thorn, K.A., 1989, Variability in the chemistry of nonvolatile organic acids downgradient of the oil body at Bemidji, Minnesota, in Ragone, S.E., and Mallard, G.E., eds., U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the Technical Meeting, Phoenix, Arizona, September 26-30, 1988: U.S. Geological Survey Water-Resources Investigations Report 88-4220, p. 35-40.

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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. Suggest reaction models by combining solution chemistry and the results of surface-alteration studies.

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

PROGRESS: (1) Isotope mass balance in Rocky Mountain Watershed: (a) Continuing investigation of the relations between isotope composition of air moisture and isotope composition of precipitation, isotope composition of evaporated soil moisture, and near-earth-surface climate parameters has yielded the following results. The near-surface vapor is modified by evapotranspired vapor. The amount of this vapor in relation to oceanically derived moisture determines the slope and intercept of the delta O-18 plot for precipitation in addition to the relation between precipitation isotope composition and climate variables. (b) Computer code for an isotope mass-diffusion model has been written. Preliminary runs of this code indicate that observed enrichment of evergreen intercepted snow can be modeled. A manuscript is nearly complete. (2) Chloride-ion mass balance studies: wet deposition of chloride-ion in the Western U.S. has been determined. Water chemistries for selected watersheds are being compiled from computer files or published literature to extrapolate methods developed in Colorado watersheds to other watersheds with a diversity of microclimates. The problem of dry deposition of chloride continues to be studied, but will require costly instrumentation if the eddy correlation-gradient method is to be used.

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. Sediments act as sources, sinks, and carriers of a variety of chemical species; to understand the processes controlling a main source of materials that enter and exit water systems, 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 chemical reactivity of the surface. 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 Raman 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 goethite type coatings. Synthesize laboratory coatings of the same materials simultaneously. 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 water having very low concentrations of dissolved solutes, and to use three-dimensional fluorescence spectroscopy to obtain definitive information on humic acid fraction patterns and augment studies of the formation of charge-transfer complexes.

PROGRESS: Seven papers and one book were published. One regional symposium on infrared spectroscopy was conducted in Denver, Colo., in August 1988. Nine abstracts were published and nine scientific talks were given at technical meetings and conferences. Fluorescence identification of geologic materials found in water and on solid surfaces was performed for and funded by White Sands Missile Range. Measurements by fluorescence spectroscopy of materials transported in the South Platte River between Chatfield Reservoir to a distance 12 miles downstream showed changes in the fluorescence pattern that were a result of changes in the transported load. This new hydrologic technique can pinpoint increases and decreases in the fluorescing materials transported by water. (Most dissolved organic compounds fluoresce.) As previously reported, abiotic photolytic reactions between sorbed organic species and substrates from iron oxyhydroxides take place with a large number of organic compounds in surface-water systems, causing oxidation of the organic species and introduction of reduced iron back to the surface water. One new facet, and an important practical consideration, is the effect of manganese in these surface-water systems. Glycolate and alanine have been used as two representative adsorbed organic materials in systematic investigations of the effects of abiotic photolytic reductions of organic materials in surface waters caused by the inclusion of manganese in the iron-oxyhydroxide (goethite) lattice. It was found that lattice manganese concentrations as low as 1-mole percent quench photolysis by 80 to 90 percent in these systems. Because manganese is distributed throughout the iron-oxyhydroxide lattice and not just at the surface, this observed ability of manganese to interfere with the surface photo-oxidation of the adsorbed organic seems to point to a resolution between two theories advanced to explain these reactions. These theories are (1) the electron transfer theory within the surface ligand complex, and (2) the semiconductor electron-hole, migration theory. The surface ligand-complex theory cannot explain the manganese effects, but the electron-hole migration theory does. Because of these results, it has been suggested to the scientific community that the electron-hole theory is correct and that manganese [Mn(II)] scavenges holes that are photogenerated in the iron-oxyhydroxide lattice, thus interfering with the surface oxidation of the organic. Distinguishing between these two theories is a fundamental scientific advancement. The ability to measure photolysis in surface waters was enhanced by including selected phenols and furfuryl alcohol, as well as n-butyl chloride, as radical trapping agents. Phenol itself, cresol, and 2.6 dimethylphenol all are sensitive to peroxyradicals in differing degrees. Furfuryl alcohol is sensitive to singlet oxygen. These studies have resulted in methods for combining the use of all three of these indexing compounds to allow one to distinguish between and measure organic peroxide, hydroxyl radical, and singlet oxygen. This represents three of the four oxidative species that are of prime importance in abiotic photochemical processes. The measurement of the fourth species, hydrogen peroxide, is well established and performed independently. Measurement of femtomolar quantities of toxic organics as well as other organic molecules in water has been described by means of "surface enhanced Raman spectroscopy" (SERS). Measurements made in this laboratory with conventional spectroscopy indicate that fluorescence interference can be overcome by use of long wavelength excitation (about 610 nanometers), and combination with SERS technology could result in a very sensitive analytical tool.

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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 based on 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 terrestrial hydrologic cycle of the Great Basin 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 to establish time-series records of climate; (3) perform real-time studies of the behavior of oxygen-18 in the hydrologic system to establish the relation between oxygen-18, lake temperature and size, and climate; (4) apply oxygen-18 climate model to core data 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 (NCAR) with ref erence to generalized surface-hydrology model of the Lahontan basin (model combines precipitation-runoff, lake evaporation, and lake thermal-evolution models); and (6) apply mesoscale calculations and generalized surface-hydrology model to determine the type of climate responsible for Pleistocene highstand lakes.

PROGRESS: Lake thermal evolution-evaporation model was validated data from the Pyramid Lake area. Radiocarbon and tephra analyses of Pyramid Lake shore core were completed. Oxygen-18 bulk time-averaged evaporation-fractionation factor was calculated for Walker and Pyramid Lakes from isotopic data. Initial winter runs of NCAR mesoscale model of Great Basin climate was completed. Large lake systems (Lahontan and Bonneville) shown to strongly affect local climate and hydrologic balance. Gas-diffusion study by Wanninkof of Lamont Doherty completed. About 40 analyses of Oxygen-18 content of vapor phase over Pyramid Lake completed. Data support estimated fractionation factor. Correlation of metprological data between land and raft stations accomplished. Three land stations was have been decommissioned. Preliminary x-ray-diffraction study of one segment of Pyramid long core was completed. Data indicate a trend in Mg/Ca ratio of carbonates with time. Synthesis of all published and unpublished lake-level data for major Great Basin lakes was concluded.

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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 aquifers 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 aquifers 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 aquifers; (2) determine the nature and role of organic carbon associated with suspended and bed sediment and aquifers; and (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, Louisiana; (2) characterize and quantify the organic compounds associated with the biota, sediments, and water by use of 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: (1) Mississippi River Study: Studies that are being conducted on the Lower Mississippi River and its major tributaries have shown for the first time that this entire river reach is contaminated by synthetic organic agrichemicals and their degradation products. Compounds such as the chlorinated pesticides partition into suspended sediments or bioconcentrate in the lipid tissues of catfish. More water-soluble compounds such as the triazine and acylamide herbicides and their degradation products exhibit relatively conservative behavior. Transport data for these compounds were collected at 17 sites during four sampling cruises. Two new industrial chemicals were reported for the first time. Trimethyltriazinetrione (TTT) (exclusively from the Kanawha and Ohio Rivers) and chloroalkylphosphate flame retardants (exclusively from the Illinois River) exhibit conservative behavior in the Mississippi River. Therefore, these compounds could serve as geochemical tracers to study mixing of these rivers below their confluences. Transport data indicate that approximately 100 metric tons of atrazine are transported into the Gulf of Mexico each year. Chlorinated compounds such as PCB's and chlordane are transported by suspended sediments. Sediment-transport data indicate a reasonable materials balance for these compounds and, hence thorough mixing of suspended sediments downstream from confluences of the Lower Mississippi and its major tributaries. (2) Calcasieu River Study: Distribution of halogenated organic compounds between water, sediment and catfish lipid tissues have shown the presence of several new polychlorinated, polybrominated, and mixed halogenated compounds. These compounds were analyzed using high resolution GC-MS; elemental compositions were determined using accurate mass measurements.

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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 (suspended matter, bottom sediment, and so forth) 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 to problems of analysis (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 problems requires an extensive research and development effort 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 use 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 analytical 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, applying statistical and factorial techniques to optimize and evaluate parametric factors; and (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 and New Fork Lakes, Wyoming, and Emerald Lake, Sequoia National Park). 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 per 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 per liter) concentrations 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 undertaken to develop a new technique for measuring the isotope ratio of potassium at trace concentration levels. A flame ionization-mass spectrometric techniques involving an air-acetylene premixed flame was developed. The technique is being used in ground-water studies at the Cape Cod Hazardous Waste Site to enploy potassium as a geochemical tracer. (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 River for polynuclear aromatic hydrocarbons. (6) Research was done on development of a technique suitable for measurement of field alkalinity by use of a microcomputer-controlled coulometric titration. (7) Research (including three field trips), was done, to measure the occurrence, distribution, and fate of trace metals in the Mississippi River system. This includes the investigation constituents, with emphasis on the of between various size fractions of suspended material (silts, colloids, and so forth). Studies were done to representatively collect and separate statistically valid and uncontaminated samples. (8) Research was done to measure the relations between hydrochemical constituents and the occurrence and distribution of benthic-invertebrate populations in river and streams. Fieldwork was done in the Gibbon and Firehole Rivers in Yellowstone National Park and streams in Catskill Mountains of New York. (9) Studies are underway to evaluate the chemical composition of ice layers in glaciers from the Wind River Mountain range in Wyoming. These studies will assist in evaluating evidence of climatic changes in atmospheric depositions.

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

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

APPROACH: Use onsite measurements of precipitation-related dissolution and damage to carbonate stone, with supplemental, well-controlled laboratory studies and reaction modeling. Conduct onsite studies involving collection of rainfall leachate solutions from an inert reference surface and from limestone and marble surfaces at five locations affected by acid rain: Chester, N.J.; Newcomb, N.Y.; Research Triangle Park, N.C.; Steubenville, Oh.; and Washington, D.C. Use data on air quality, meteorology, rainfall and rain-runoff quality and changes in chemical composition of limestone and marble to develop a quantitative description of carbonate stone dissolution and damage due to acid rain and air pollution. Use laboratory studies and reaction modeling to identify processes involved in acid rain damage and dissolution due to acid rain.

PROGRESS: Five years of intermittent onsite measurements of acid rain weathering of limestone and marble have been completed at five research sites in the eastern United States. The experimental protocol has been modified to assess the importance of rock wetness, rock orientation, and within-storm variation in rainfall chemistry on carbonate rock weathering. Results of program have been summarized in a paper published in Earth Surface Processes and Landforms. Carbonate stone weathering rates have been quantitatively related to acid deposition and natural processes.

REPORTS PUBLISHED:

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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 whereas 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 of 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 that 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: Fundamental studies of the acid-group structures in aquatic fulvic acid isolated from the Suwannee River, Georgia, revealed significant amounts of substituted malonic acid structures. This discovery is significant in explaining certain trace-metal complexation characteristics of natural organic solutes, and it also explains the biogeochemical pathway to certain components in aquatic fulvic acid. Significant concentrations of glycoprotein colloids were found in the Mississippi River and major tributaries where autochthonous production was significant. These glycoproteins may be significant in suspended-sediment aggregation processes, and they may also facilitate the transport of certain trace metals. Detergent components found in ground water at the Cape Code Hazardous Waste Site were isolated and fractionated into LAS parent compounds, LAS degradation products, and nonionic surfactant degradation products. Laboratory studies of adsorption of chlorinated benzene contaminants onto aquifer-core sediment constituents were completed; this work will be the basis for Larry Barber's Ph.D thesis.

REPORTS PUBLISHED:

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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 rather 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 processes that control the movement of colloids through different types of aquifers have 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 a better understanding of the processes 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 processes controlling sorption of materials onto colloids; (5) study the processes that control the movement of colloids in surface-water and ground water; and (6) On the basis of 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 using 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). Separate the highly polydisperse colloidal samples into less complex mixtures by use of these techniques, which are more readily amenable to our other analytical techniques.

PROGRESS: Project personnel have participated in a total of four research cruises on the Mississippi River. Analysis of material suspended in the river indicates that the sediment is composed of greater than 50 percent colloidal material, with a large percentage of disaggregated colloidal material. The effective surface-area flux moving past St. Louis, Mo., is in excess of $1x10^{12}$ square meters per day. The project is also involved at the Upper Arkansas River site at Leadville, Colo. Initial results indicate that iron removal from that stream, which is contaminated by acid mine drainageis as a result of rapid precipitation of 50 nanometer iron hydroxide colloids, followed by rapid aggregation into submicron particles, then ultimately by slow agglomeration of the aggregates into larger particles that either settle or are scavenged by cobbles in the stream bed. Five papers describing results of these studies have received Director's approval for publication this past year and have been accepted by various journals or books for publication.

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CR316	Solid- Phase Chemistry

TITLE: Solid Phase Chemistry and Related Environmental Processes

PROJECT NUMBER: CR 89-316

LOCATION: Colorado

PROJECT CHIEF: Seeley, James

HEADQUATER OFFICE: Lakewood, CO

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

OBJECTIVE: (1) Define the processes involved in and governing metal transport between sediments and surrounding waters. Characterize the chemistry and chemical reactions at the sediment-water interface and supporting substrates in samples from pristine and polluted environments. Define the chemical and physical changes that occur at the surface of sediments subjected to changing aqueous environments.

APPROACH: Develop techniques for the collection and preservation of sedimentary materials for subsequent surface-chemistry and related chemical-reaction studies. Characterize sediments by use of solid-phase surface-analysis systems, that is, electron spectroscopy for chemical analysis (ESCA), Auger electron spectroscopy (AES), and secondary ion mass spectrometry (SIMS). ESCA is performed by energy analyzing photoelectrons emmited from a solid surface as a result of x-ray excitation, and identification of chemical states resident in that surface can be made from precise determinations of binding energies, peak shapes, and other spectral features. Auger (AES) techniques are extremely surface sensitive and are ideal for applications by which the distribution of surface constituents must be determined with high spatial resolution and several monolayer surface sensitivity. All elements (except H and He) present in the outer few atomic layers of a material can be identified with AES. SIMS is a surface-analysis and depth-profiling technique used for studies of trace-elemental surface chemistry because it offers extremely high detection sensitivity. SIMS also provides isotopic and molecular information. Sediment material from natural aquatic systems, polluted and nonpolluted, will be examined. Laboratory studies of selected natural and standard reference sedimentary materials will be made to determine the initial surface chemical composition and to follow the chemical reactions as the solid-phase materials are subjected to changing aquatic environments.

PROGRESS: Began to develop laboratory facility. Purchased and installed instrumentation for solid-phase surface analysis and metal constituents in waters.

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 are only estimated when biogeochemical cycling and ecological responses are being considered. Understanding geochemical processes that control nutrient and transition metal chemistry of natural waters is requisite for predicting the effects that human-induced events will have upon natural geochemical cycles and for determining the use of natural waters as a resource (for example, estuarine waters as food resources).

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

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

PROGRESS: (1) Research continues into the arsenic geochemistry of rapidly accumulating sediments in Lake Oahe, South Dakota. Several meter-long cores were analyzed for interstitial-water and solid-phase arsenic species. Generally, arsenic (V) was the predominant species in surficial, oxidized sediments. In deeper, more reducing sediments, interstitial arsenic (III) is the dominant species. Solid-phase arsenic species distributions show approximately equal quantities of arsenic (III) and (V). In sediment sections that exhibit a dark gray to black color, solid-phase arsenic (III) predominates but coexists with some residual arsenic phase that probably contains sulfide. Interstitial-water chemistry, solid-phase sulfur data, and SEM photomicrographs indicate that these sediment intervals contain iron-arsenic-sulfur phases that probably formed authigenically as a result of microbial sulfate reduction. However, the presence of some residual arsenic sulfide phase in surficial oxidized sediments indicates that detrital metal sulfides may be present as well. (2) Research also continues on a 2-meter core from Lake Oahe, South Dakota. The Cs-137 distribution indicates that the sedimentation rate has been decreasing from 1959, when the reservoir was formed, to the present. Subsequent Pb-210 analyses confirm the variable-sedimentation-rate model. Geochemical analyses of 2-centimeter sections sampled throughout the length of this core have yielded some interesting results. On the basis of the Cs-137 distribution, a detailed chronology of geochemical and climatic events was constructed. Sedimentary calcium is a tracer of easily erodable Badlands deposits in the Cheyenne River basin, and a comparison between calcium and quarterly flow of the Cheyenne River results in a strong positive correlation. On the other hand, there are strong inverse correlations between quarterly flow and manganese, cobalt, and vanadium. These elements are redox sensitive and tend to concentrate as oxides on sediment particles near the sediment-water interface during periods of low flow when the sediment influx is low. (3) Studies continue on the sedimentary geochemistry of Pueblo Reservoir, south-central Colorado. A paper published in the 1989 proceedings of the U.S. Geological Survey Toxic Substances Hydrology Program Technical Meeting in Phoenix, Arizona, describes some results of solid-phase analyses of sediment cores. The vertical distribution of normalized heavy-metal data shows pronounced peaks at depth that may record significant inputs of Pb, Cd, and Zn from acid mine drainage in the Upper Arkansas River Basin. (4) Monthly net fluxes into and out of the water column of Pueblo Reservoir for 1986-87 were calculated for chloride, sulfate, total P, dissolved P, total iron, and total managenese by use of a box-model approach. The net flux is taken to mean the net sum of all source and sink processes acting on a constituent over a period of time. In the following discussion a negative net flux represents a net loss, wh ereas a positive value represents a net source for a particular constituent from the reservoir water column. The data used for these calculations were obtained from a 3-year study (1986-88) in the Pueblo Reservoir conducted by Pat Edelman of the WRD's Pueblo Subdistrict Office. With only one exception, the annual pattern for the net fluxes for all constituents was for the most negative fluxes to occur in June and July, corresponding to the months of the greatest freshwater input to the reservoir. The net fluxes calculated for chloride and sulfate were positive except for the months of June and July, whereas those for total iron and total phosphorus were all negative. The net fluxes for manganese were equally divided between positive and negative values and showed the least annual variation of all constituents considered. (5) Sediment traps were deployed at two depths at three stations in the Pueblo Reservoir in August and October of 1988 and monthly starting in April 1989 to directly measure particle fluxes and to collect material for subsequent analyses and calculation of downward fluxes of individual constituents. To date, only sediment-particle fluxes have been determined for the deployments in August and October 1989. Those results show unexpectedly high sediment fluxes compared to estuarine sediment fluxes measured in the Potomac Estuary with the same sediment-trap design. With the limited data available there is little evidence of longitudinal variation in sediment fluxes; however, if all data are pooled, there is a close fit of measured sediment fluxes with the depth of the sediment trap from the reservoir surface. This implies that sinking particles collected by the traps may be uniformly distributed in the water column. Because August and October are months with very little freshwater input to the reservoir, the sinking particles are probably locally produced and not transported into the reservoir by the river. (6) Participation in the SCOPE (Scientific Committee on Problems in the Environment) Carbon Program has resulted in a paper entitled "Depositon of Organic Carbon in Upper Missouri River Reservoirs" to be published in 1989 as Part 6 of the series entitled "Transport of Carbon and Minerals in Rivers, Lakes, Estuaries and Coastal Seas." Sedimentary organic carbon accumulates in three upper Missouri River reservoirs at rates that vary from 190 to 230 grams jof carbon per square meter per year. The deposition and subsequent accumulation of sedimentary organic carbon is suported primarily by calculated plankton photosynthesis. One reservoir appears to represent a situation where allochthonous organic carbon transported in from the drainage basin constitues a significant fraction of the carbon that accumulates in bottom sediments. The rapid bulk-sediment accumulation rates that commonly occur in reservoirs may reduce substatntially the diagenetic remobilization of deposited organic carbon because organic matter is buried in botton sediments long before diagenetic reactions are complete.

REPORTS PUBLISHED:

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Shultz, D.J., 1989, Nitrogen dynamics in the tidal freshwater Potmac River, Maryland and Virginia, Water Years 1979-81: U.S. Geological Survey Water-Supply Paper 2234-J, 41 p.

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: The solubilization and subsequent resorption of radionuclides by ore components or by reaction products during the milling of uranium ores can have both economic and environmental consequences. Particle-size redistribution of radium during milling has been demonstrated by previous investigators; however, the identification of sorbing components in the tailings has received little experimental attention. In this study, uranium-bearing sandstone ore was milled, on a laboratory scale, with sulfuric acid. At regular intervals, filtrate from this suspension was placed in contact with mixtures of quartz sand and various potential sorbents that occur as gangue in uranium ores; the potential sorbents included clay minerals, iron and aluminum oxides, feldspar, fluorspar, barite, jarosite, coal, and volcanic glass. After equilibration, the quartz sand-sorbent mixtures were separated from the filtrate and radioassayed by gamma spectrometry to determine the quantities of ^{238}U, ^{230}Th, ^{226}Ra, and ^{210}Pb sorbed, and the radon emanation coefficients. Sorption of ^{238}U was low in all cases, with maximal sorptions of 1 to 2 percent by the bentonite- and coal-bearing samples. Thorium-230 sorption also was generally less than 1 percent; maximal sorption here was observed in the fluorspar-bearing sample and was accompanied by the formation of gypsum. Radium-226 and ^{210}Pb generally showed higher sorption than the other nuclides--more than 60 percent of the ^{226}Ra solubilized from the ore was sorbed on the barite-bearing sample. Radon emanation coefficients of the samples ranged from about 5 to 30 percent, with the coal-bearing samples clearly demonstrating an emanating power higher than that of any of the other materials.

REPORTS PUBLISHED:

Landa, E.R., Miller, C.L., and Brich, R., 1988, Radioactive and nonradioactive solutes in drinking waters from radon-charging devices: Health Physics, v. 54, p. 99-106.

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

OBJECTIVE: Evaluate local and global carbon fluxes associated with hydrologic and geologic processes. Investigate the possibility of past variations in the world's (natural) CO_2 balance and apply this information to the prediction of future global CO_2 fluxes. Understand the role of fluxes of 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 from direct measurements, published literature, and computer models of hydrologic and geologic processes. Use gas chromatography, high performance liquid chromatography, potentiometric titration techniques and other analytical methods. Acquire stable-isotope and ^{14}C measurements where appropriate. Use available data to constrain computer models on the basis of chemical thermodynamic and kinetic relationships and the conservation of mass and charge.

PROGRESS: Project activities have focused on aspects of the carbon cycle that are particularly relevant to the geochemical effects of CO_2 and to long-term geochemical predictions. Matrix transformations and eigenanalysis show how carbon-cycle models appropriate to short time scales can be systematically related to models appropriate for long time scales. To analyze the sediment record of carbon-cycle change, and to assist in long-term CO_2 predictions, modeling techniques have been developed to accommodate carbonate dissolution and other sediment interactions. Ocean-atmosphere-sediment modeling indicates that, if all of the world's fossil fuel reserves are burned, the average lysocline and atmospheric CO_2 concentration may remain perturbed for thousands to tens of thousands of years. These model results are consistent with a significant correction of previous analyses of the whole-ocean carbonate-ion response to perturbations. On the basis of geologic record of oceanic carbonate dissolution, the model also indicates that geologic variations in atmospheric CO_2 must have been accompanied by significant oceanic alkalinity changes. In the laboratory, gas chromatographic techniques have been implemented for analyzing carbon dioxide and methane in 1-millileter soil gas samples. An automated remote soil gas sampler is being readied for field testing. This project has also contributed substantially to bureau and Division climate program development.

REPORTS PUBLISHED:

Sundquist, E.T., 1988, The greenhouse effect and global warming, in Lins, H.F., Sundquist, E.T., and Ager, T.A., eds., Information on selected climate and climate-change issues: U. S. Geological Survey Open-File Report 88-718, p. 11-21.

Sundquist, E.T., in press, Long-term aspects of future atmospheric CO_2 and sea-level changes, in Revelle, R., ed., National Academy of Sciences volume on sea-level change: Washington, National Research Council.

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 can regulate reaction pathways and products. Knowledge of the geochemical behavior and cycles of trace elements and nutrients is essential for understanding and predicting the consequences of deliberate or accidental anthropogenic additions of these substances to the environment.

OBJECTIVE: Define the effects 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) ultracentrifugation 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 by use of 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: Investigations of biogeochemical processes in small forested watersheds are continuing. Results of analysis of stream chemistry for 69 streams in Virginia and Maryland indicate that the chemistry of these streams is strongly controlled by mineral-weathering reactions throughout the year. Alkalinity was shown to be highly dependent on the reactivity of bedrock within the watershed. A geology-based method was developed for predicting the sensitivity of streams in the Blue Ridge Physiographic Province in Maryland to acidification by acid deposition. This method is being extended to other geologic terrains. A systematic relationship between landscape position, drainage characteristics, and clay mineral assemblages in several eastern USA watersheds was identified. It was found that hydroxy-interlayer vermiculite plays a significant role in regulating the concentration of of Al^{+3} in acidic surface waters in a watershed in the eastern United States . Studies of SO_4^{2-} dynamics at the Patowmack Farm site showed that SO_4^{2-} is strongly retained in the watershed, and that little or none present in groundwater. Sulfate appears to be retained in clay-rich mineral soil horizons. Deposition of NO_3^- relative to SO_4^{2-} is higher at the Patowmack Farm site than other monitored watersheds probably as a result of automobile emissions in the Northern Virginia region and oxidation of NH_4^+ to NO_3^- after fertilizer applications to the surrounding farmland. This was also apparent in the less than 2:1 SO_4^{2-} to NO_3^- ratio in throughfall; positive net fluxes indicate that NO_3^- is deposited to the forest canopy in excess of plant needs or ability to absorb. Biotite dissolution kinetics and dissolution mechanisms are being investigated in the laboratory under a range of pH and Eh conditions. A major increase in solution rate occurs between pH 3 and pH 4. Preliminary data indicate a change in the mechanism of dissolution at low pH. The reaction is less sensitive to changes in redox condition than to change in pH.

REPORTS PUBLISHED:

Bricker, O.P., and Rice, K.C., 1989, Acid deposition to streams--a geology-based method predicts their sensitivity: Environmental Science Technolology, v. 23, p. 379-385.

Puckett, L.P., 1988, Biological, chemical, and physical factors controlling the chemistry of throughfall precipitation: Fairfax, Va., George Mason University, Ph.D. dissertation.

Olson, C.G., 1988, Clay-mineral contribution to the weathering mechanisms in two contrasting watersheds: Journal of Soil Science, v. 39, p. 457-467.

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 determination of the toxicity of metals in these systems are dependent on metal speciation. An example of an environmental problem involving organo- metal associations is the spread of toxic metals with the transport of sedimentary material. The presence of organic coatings on sedimentary matter and the large surface area per unit weight of small sediment particles result in high metal concentrations in the small-particle fraction. These small particles are more easily transported by the water column than are coarser sedimentary material. This mobility means that toxic metals can extend beyond a point source. How environmental changes affect the partitioning and speciation of metals, and the rate at which these changes occur, needs to be evaluated.

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

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

PROGRESS: An objective of this project is to determine the processes that lead to the transport and fate of heavy metals in aqueous environments. A primary concern is metals that are toxic to living organisms. The determination of the phase with which the metal of interest is associated is crucial to understanding its transport, fate and bioavailability. Metals associated with organic compounds are labile (that is, vulnerable to release) by degradation of the organic phase under both oxic and anoxic conditions. On the other hand, metals associated with metal oxides are labile under reducing conditions only. It is important to know the phase association of metals to be able to predict if release to the solution phase of heretofore immobilized metal can occur in both the water column (oxic conditions) and sediment (anoxic conditions) or if release would be expected to occur only in the sediment. Two activities this year contributed to an understanding of the phase association of metals. A statistical evaluation of chromium, iron, and manganese data from a comparative study of metal-extraction techniques revealed that metal concentration data obtained by the method used by the WRD's National Water Quality Laboratory for recoverable metals should be compared with extraction data obtained with hydrogen peroxide plus pyrophosphate, a minor modification in the WRD method, and with total metal concentrations to estimate the amount of metal associated with both the organic and inorganic phases. A second finding resulted from the initiation of the use of inexpensive ultrafiltration units which can be used with small volume water samples that are to be filtered in the field. Data from a cooperative field study (with the U.S. Environmental Protection Agency) of the Calcasieu River estuary, Louisiana, June 1989, showed that chromium in the water column at several sites was associated with colloidal-size iron oxides in the water column. Preliminary evaluation of the data shows that the data on total ammonium in sediment and on suspended particulate metal correlate with the U.S. Environmental Protection Agency's identification of sites with high mortality of test organisms. The ammonium data was obtained using a very easy, novel application of the ammonia electrode in which total sediment ammonium is determined with an ammonia electrode at the field site. Total ammonium concentrations in sediment are a measure of the degree of organic degradation occurring in the sedimentary material. The need for a better understanding of the association of heavy metals with naturally occurring organic matter has led to a cooperative study with a university chemistry department in which supercritical fluid extraction is being applied to separate organic compounds from environmental samples to provide material suitable for structural characterization. A report from a previous study of nitrogen cycling in the Potomac River estuary has been accepted for publication. Several interpretative reports that include metal-concentration data from the sediments of the Calcasieu River estuary have been prepared and have received Director's approval.

REPORTS PUBLISHED:

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Simon, N.S., 1989, Nitrogen cycling between the sediment and the shallow-water column in the transition zone of the Potomac River and Estuary, II. The role of wind-driven resuspension and adsorption of ammonium: Estuarine, Coastal and Shelf Science, v. 28.

Simon, N.S., 1989, Phase association of trace metals in sediments from the Calcasieu River, Louisiana, in Mallard, G.E., and Ragone, S.E., eds., and Ragone, S.E., U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the Technical Meeting, Phoenix, Arizona, September 26-30, 1988: U.S. Geological Survey Water-Resources Investigations Report 88-4220, p. 301-308.

NR142 ORGANIC CONTAMINANTS IN WATER

TITLE: Organic Contaminants in Water

PROJECT NUMBER: NR 88-142

LOCATION: Topical Research

PROJECT CHIEF: Baker, Robert A.

HEADQUARTERS OFFICE: John C. Stennis Space Center, MS

PROBLEM: The chemical, biological and physical factors affecting distribution of contaminants in water are generally poorly defined. This is especially true if the contaminants are associated with sediments and are organic in origin. Further complication exists because the sampling and preanalytical procedures are not universal and must be developed for each case under study. Variations in methodology often preclude comparison of results from different studies. The fate and transport of the organic contaminants is a critical factor in water resource management decisions.

OBJECTIVE: Make critical assessment of the existing and developing state-of-the-science for sampling, preanalytical processing, and analysis of organic contaminants in water, with emphasis on sediment-borne contaminants. Issue recommendations for general practice and specific techniques evolved for ensuing research. Define, through laboratory and field studies, the relative effects of chemical, biological, and physical factors on the fate and transport of organic contaminants associated with particulate matter in water. Use results to write algorithms for water-quality models for resource managers.

APPROACH: Develop recommendations for general practice and specific techniques identified for project research. Conduct laboratory studies of organic-contaminant stability under varying chemical, biological, and physical conditions. Use specific organic constituent(s), highly-characterized sediments or soils, and well-defined aqueous systems to measure organic stability. Separate the highly correlated chemical and biological factors by sterile procedures when appropriate.
PROGRESS: A major symposium has been organized to be held at the National Meeting, American Chemical Society, Boston, April 22-27, 1990.

Internationally known scientists will contribute to a highly interdisciplinary program, "Organic Substances and Sediments in Water." The program will include new research results, critical assessment of current knowledge, and recommendations for further priority research. A concomitant critical literature review is underway.

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 water and solids, especially in the case of minor elements. Thus, when new solutes are added to a stream, they can behave as conservative constituents, be adsorbed by stream solids (with or without displacement of previously adsorbed materials), precipitate, or combine with stream solutes to form complexes having properties quite different from those of the original solutes. In some respects, stream biota will behave much like abiotic solids in reacting with stream solutes, but in other aspects, the behavior of stream biota can be very different as, for example, in the case of nutrient uptake. A better understanding of the rate and nature of interaction between water and stream solids 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 on their chemistry and the nature of the stream solids (sediments and biota) with which they are interacting.

PROGRESS: (1) Soil was infiltrated by water containing relatively large amounts of deuterium and oxygen-18. Resulting isotope ratios in near-surface soil water were approximately 1800 for delta deuterium and approximately 100 for delta oxygen-18. After a warm month with no rainfall on the soil, a core was taken and segmented into approximately 1-centimeter layers. The top few layers showed a major decrease in delta values rather than an increase, which would be expected if only evaporation had occurred; therefore, exchange with atmospheric moisture is presumed to have been more important than evaporation in controlling the isotopic composition of near-surface soil water. Such a process may be significant in some areas in causing soil water displaced by rainfall downward to the water table to differ from the average isotopic composition of rainfall. The research was done with the assistance of Carol Kendall. (2) Work continued with a committee on sedimentation activities in the Water Resources Division. An official consulting trip to the People's Republic of China was made. A report on solute transport during rising discharge after a low-flow period is ready for colleague review.

REPORTS PUBLISHED:

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Triska, F.J., Kennedy, V.C., Avanzino, R.J., Zellweger, G.W., and Bencala, K.E., in press, Retention and transport of nutrients in a third-order stream in northwestern California--channel processes: Ecology, v. 70.

in press, Retention and transport of nutrients in a third-order stream in northwestern California--Hyporheic processes: Ecology, v. 70.

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 can 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.

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. Research results from this project are used 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.

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: During FY 1989, research was completed on the coprecipitation of copper, nickel and cadmium with manganese in aerated solutions over a range of pH from 8.0 to 9.0. The rate of oxidation and average oxidation number of manganese precipitated in these experiments were both increased by the accessory metals, the strongest effects being produced by cadmium and the weakest by nickel. A part of the cadmium was precipitated as a mixed oxide having the formula $Cd_2Mn_3O_8$ in which all the Mn is in the 4+ oxidation state, this oxide was identified by electron microscopy and x-ray diffraction. The standard free energy of formation of the oxide was determined to be -448.3 plus or minus 1.5 kilocalories per mole. The copper analog of this oxide, $Cu_2Mn_3O_8$, was also identified by electron microscopy, but is less stable than the cadmium-containing form. The effect of nickel on the manganese oxidation process appears to be explainable as the result of substitution of Ni^{2+} for Mn^{3+} in the MnOOH crystal lattice that destablizes the structure and encourages formation of Mn^{4+} by disproportionation of two other Mn^{3+} ions. Work was continued in cooperation with the Geologic Division, Reston, to measure thermodynamic stability of duplicate clay-mineral samples by calorimetric and solubility techniques. The project staff member assigned to this work was transferred during the year to the Clay-Water Reaction Project in Denver, Colo. Preliminary studies in the laboratory identified kutnahorite, a dolomite-type mineral containing Mn^{2+}, (Mn, Mg) $Ca(CO_3)_2$ as a component of precipitates formed along with Mn_3O_4 by raising the pH and aerating water from the perennial-flow reach near the lower end of Pinal Creek. Whether this carbonate is formed in the aquifer feeding the creek is not yet known.

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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 from 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 by use of the PRMS to estimate the effects 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 various physiographic and climatic regions of the United States; evaluate the PRMS components with regard to the significant hydrologic processes in each region and enhance selected components through modification and additional research where required; assess the sources of model error and the transfer of these errors to the model output; evaluate the 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 these rates to hydrologic and ash characteristics.

PROGRESS: Conversion of the PRMS to a fully modular watershed-modeling system incorporating graphical interfaces, expert systems, digital terrain analysis, and geographical information system output was continued. Evaluation and enhancement of the snowmelt-runoff simualtion capabilities of PRMS in different climatic and physiographic regions was expanded from nine basins in the United States to include additional basins in India and China. Objective procedures to delineate watershed boundaries and to characterize hydrologic response units within watersheds were tested by means of digital terrain-analysis techniques. Procedures to register remotely sensed digital records of snow-covered area to watershed characterizations were developed, and results were compared with PRMS-simulated snow-covered area. Simulated and observed snow-covered areas were very similar in space and time. An operational weighted least-squares regression procedure that reduces sampling variability in estimates of the parameters used to quantify the variance of t-year flood estimates was developed and evaluated by means of data from 200 small basins in 12 Central and Southeastern states east of the 105th meridian. Hydraulic research was expanded to include instream studies at the Rocky Mountain Hydraulics Laboratory near Allens Park, Colo. Studies will assess the complexities of hydraulics in mountain rivers, and the results will be used to improve hydraulic models. New paleohydrologic research was begun to assess the effects of climate changes during the Holocene on flood hydrology in the Front Range in Colorado. Current paleoflood research has improved the the ability to estimate the frequency of catastrophic floods. The hydraulic characteristics of the surface of a glacier were measured. These results are applicable to a broad range of glaciers in different regions and provide empirically verified parameters for this aspect of glacier runoff. A theory was proposed to explain glacial floods from glaciers with no observed reservoir of water. A new system to automatically measure and record tracers injected into a flow system was developed.

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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 overdesign and underdesign 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 the instantaneous unit hydrograph (IUH) 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 incorporate results in geomorphology for the so-called random topology model and results in probabilistic branching theory. Other properties of the random topology model have been investigated, including the probability distribution of the network width function and mainstream-area relations. Extension have been made to nonlinear channel routing schemes by use of simulation techniques, and the connection of basin-scale relations to relations obtained by traditional regionalization methods have been explored. In addition, 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 that have been obtained for naturally occurring networks.

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

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

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

PROGRESS: (1) The fate of acetone in an outdoor model stream with a nitrate supplement was investigated to determine if a nitrate limitation was the explanation for the failure of acetone to undergo bacterial degradation in a previous experiment. Significant bacterial degradation did not occur in the model stream, contrary to expectations based on laboratory studies of model-stream water enriched with nitrate. A possible explanation was the limited residence time of the outdoor model stream. (2) A study of the trihalomethane formation potential in the

Kentucky River was initiated in conjunction with the National Water-Quality Assesment project. Preliminary results indicate that the formation of the trihalomethanes is strongly dependent on the dissolved organic carbon content of the water and on water temperature. Some dependence on pH and the initial free chlorine concentration was observed. Bromide ion in the water, which apparently originated from the oil and gas fields in the upper part of the basin, resulted in the formation of brominated forms of the trihalomethanes at certain times of the year.

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Rathbun, R.E., 1989, Discussion of "Effect of temperature on oxygen transfer--laboratory studies": American Society of Civil Engineers Journal of Environmental Engineering, v. 115, no. 2, p. 482-484.

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 qualitatively and quantitatively. Design of the desired simulation models depends in large measure on accurate mathematical-numerical representation of the hydrodynamics of the transient-flow process.

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

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

PROGRESS: (1) Continued analysis of the nonhomogeneous terms in the unsteady flow equation set used in BRANCH, the one-dimensional, network flow model and, together with colleagues, subsequently reported findings of friction resistance at International Conference on Channel Flow and Catchment Runoff. (2) Studied the problems of inputting time series of boundary-value water-level and transport information derived from a regional, small-scale, two-dimensional model to a local, large-scale submodel "nested" within the regional model. Determined that although the transfer of boundary-value data is relatively uncomplicated as long as the orientation of model grids is the same, transfer does become complex and tricky when rotation of the fine grid (large scale) submodel is permitted with respect to the regional, coarse-grid, model. (3) Worked with a colleague to modify the Time Dependent Data System (TDDS) and Time Dependent Data Base (TDDB) to incorporate the capability for a universal, latitude/longitude-based site identification. Achieved operational status with new version of TDDS/TDDB that will accept either the traditional 8-digit site identification number or the universal site-identification. Extensively edited and expanded documentation for TDDS/TDDB in preparation for publication. Wrote several routines to take full advantage of the newly incorporated capabilities in TDDS/TDDB. (4) Devoted considerable time and effort to "rethinking" and transforming SIMSYS2D (two-dimensional, flow-transport modeling system) for operation on the PRIME minicomputers or super microcomputers. Worked with another Federal agency to achieve up-to-date graphics capability for SIMSYS2D. (5) Continued development of methodology for implementing two- and three-dimensional models by use of digital line graph data and digital land-use/land-cover data obtained from various geographical information systems. Prepared and presented results of one such investigation at National Conference, American Society of Civil Engineering. Pioneered analysis of model output results by use of ARC/INFO. Evaluated the development and implementation of a three-dimensional flow/transport model. Provided project consultation, assistance, and (or) instructions to several District offices planning or already using one- and two-dimensional modeling techniques devised by this project and by colleague members of the Surface Water Physics research group.

REPORTS PUBLISHED:

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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 the WRD 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. In addition, relatively few people are aware that present-day computer modeling requires much broader knowledge and techniques than does 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 effects that changes in numerical schemes and modeling methods have on simulation results. Compare relative merits of different methods and techniques from various viewpoints. (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: (1) As a continual investigation on nonhomogeneous terms in the partial differential equations describing unsteady open-channel flows, intensive study was made on the characteristics of frictional slope term. A series of numerical experiments resulted in significant findings and very useful suggestions and guidelines to model developers and users. (2) Two multimode schemes for flow simulation by the method of characteristics (MOC): (a) multimode MOC of the first kind--a scheme that includes the implicit, temporal reachback, spatial reachback, and classical modes. The model based on this scheme was improved, expanded, and applied to several river reaches; and (b) multimode MOC of the second kind--another new numerical scheme that includes the spatial reachout, temporal reachout, spatial reachback, temporal reachback, and classical modes. Its model capacity is about the same as the preceding one, but it requires much less programming effort and computer time. (3) Modeling unsteady alluvial-channel (movable-bed) flow by the multimode MOC. The model is a genuinely coupled unsteady flow-sediment transport model, capable of simulating a class of unsteady flows having flow reversal, lateral sediment inflows, nonprismatic channel, and other complex conditions. It was further identified that the model could be properly scaled, as in a physical scale model, to allow separate calibration of flow-resistance coefficient and sediment-concentration coefficient, as well as simulation of different types of flow in varied scale zones. (4) Numerical stability and accuracy analyses were performed on biradial and triradial multimode MOC. The results are useful in affording modelers the insight and confidence to this new method. (5) A systematic study of multiradial multimode MOC, which is underway, would lead to effective numerical modeling of time-dependent surface-water flows such as nonhomogeneous-density flow, stratified flow, and so forth.

REPORTS PUBLISHED:

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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 by means of mathematical-numerical simulation models. To accurately simulate temporal and spatial variations of flow, which significantly define the transport processes, the simulation model must be capable of accounting for hydraulic and tide-induced fluctuations, water withdrawals, discharges, winds, nonuniform geometric configurations, and other human-induced or natural factors.

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

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

PROGRESS: (1) Recent modifications and extensions of the unsteady-flow equations and the branch-network model now allow for full accounting of time-varying overbank-storage, nodal-inflow, and wind-stress conditions typically encountered in open-channel systems. The branch-network matrix-solution method has been modified to permit explicit specification of external boundary conditions by equation. (2) An investigation into the interrelation and numerical treatment of nonhomogeneous terms representing bed slope, frictional slope, nonprismatic geometry, lateral flows, and wind stress in the unsteady-flow equations has been conducted, and a set of recommendations for model development and implementation have been reported at a national hydraulic engineering conference. A comprehensive set of numerical experiments has been conducted to analyze various methods of boundary-condition treatment for improved numerical solution of the unsteady-flow equations and for proper model implementation. Results indicating highly varied degrees of response for different boundary-condition combinations have been reported at an international society conference. (3) A two-dimensional hydrodynamic/transport model has been analyzed to develop and demonstrate techniques for evaluating tidal hydrodynamic, circulation, and transport changes due to highway crossings in estuarine wetlands and through riverine floodplains. Findings pertaining to the use of refined, nested submodels to resolve local flow conditions and the effects of refined temporal and spatial resolution on solution results are to be presented at a national society conference. (4) A research report by Lee and Froehlich and a user's manual by Froehlich were completed to conclude the project "Two-Dimensional Finite-Element Hydraulic Modeling of Bridge Crossings," conducted for the Federal Highway Administration. A two-dimensional, finite-element flow model--widely used by WRD personnel, other Federal and state agencies, university researchers, and private consultants--evolved from this project effort. A report of the proceedings of the Advanced Seminar on One-Dimensional Open-Channel Flow and Transport Modeling has been prepared and approved for publication.

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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 WRD'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 monthly flow model of the Delaware River was developed to evaluate the effects of climate change on water availability in the basin. Preliminary results indicate that an increase in average temperature of 2 or 4 degrees Celsius would result in a significant increase in drought risks. Progress also was made in a comparison of network-design techniques for the World Meteorological Organization. A program to compare two methods was modified to work with data from Australia and other countries. Results show that the generalized-least-squares method developed under this project performed as well or better than the method to which it was compared.

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NR133 REGIONAL HYDROLOGIC PROCESSES

TITLE: 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 characteristics. Inferences have been attempted by regressing the measures of hydrologic interest against such characteristics. Such treatment has been insufficient to fully explain the variations or extremes in discharge patterns observed within a geographic area. Long-term influences such as decadal to centennial climatic fluctuations need to be considered, and the stochastic structure of the hydrologic process itself needs to be studied.

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

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

PROGRESS: (1) Extensive time series analysis in both the frequency and the time domain of a isotopic/proxy climate record of several hundred thousand years from the Great Basin (Devil's Hole) has been performed to study what characteristic frequency signals can be deduced. (2) In collaboration with colleagues in Branch of Regional Research--Western Region, the Office of Surface Water, and each District office, the construction and assemblage of a hydroclimatological discharge data set is nearing completion. (3) Analysis of spatial patterns of hydrologic extremes in the United States since the beginning of this century is being analyzed in connection with the development of a video tape (in collaboration with the Office of the Assistant Chief Hydrologist for Scientific Information Management, Hydrologic Information Unit).

REPORTS PUBLISHED:

Cayan, D.R., Gardner, J.V., Landwehr, J.M., Namias, J., and Peterson, D.H., 1989, Introduction, in Peterson, D.H., ed., Aspects of climate variability in the Pacific and the western Americas: Washington, D.C., American Geophysical Union, Geophysical Monograph 55, p.xiii-xvi.

Landwehr, J.M. and Slack, J.R., 1990, HCDN (Hydro-Climatic Data Network)--a U.S. Geological survey discharge data set for climatological impact analysis in Symposium on Global Change Systems, Special Sessions on Climate Variations and Hydrology, Proceedings: American Meteorological Society.

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.

NR144 Hydrology in Atmospheric GCM's

TITLE: Water and Energy Balances of the Land Surface in Atmospheric General Circulation Models (GCM's)

PROJECT NUMBER: NR 88-144

LOCATION: Topical Research

PROJECT CHIEF: Milly, Chris D.

HEADQUARTERS OFFICE: Reston, VA

PROBLEM: The climate, hence the water balance, of the Earth's continents is influenced much by the hydrologic behavior of the continental land surfaces. Improved reliability of climate models is believed by many researchers to be hindered by inadequate parameterization of the land hydrology in atmospheric general circulation models (GCM's). Recent work in this area has raised new questions regarding model sensitivities and robustness of model results in view of increased model complexity.

OBJECTIVE: (1) Assess the validity of the existing parameterization of land processes in the GCM of the Geophysical Fluid Dynamics Lab (GFDL). (2) Determine the sensitivity of land water and energy balances for land to the various assumptions made in formulating the GFDL and similar parameterizations. (3) Modify the parameterization, as appropriate, to represent land processes more faithfully. (4) Employ the GFDL GCM, coupled to a realistic surface model, for studies of climate, hydrology, and climatic change.

APPROACH: Formulate a successively refined family of models for the description of land surface water and energy balances, starting from the orginal GFDL bucket model. Employ these models off-line and in conjunction with the GFDL GCM to study the questions of sensitivity and of global water and energy balance. Carry out refinement and sensitivity analysis in an iterative, interactive mode.

PROGRESS: (1) The GFDL GCM land surface parameterization has been studied and generalized. (2) A dimensionless framework for off-line analysis of land-surface parameterizations has been developed. (3) Off-line analyses of the generalized parameterizations have revealed important sensitivities not fully recognized heretofore in the GFDL GCM. For example, the GFDL formulation for potential evaporation (and that of other GCMs) exaggerates the rate of soil-moisture depletion during the dry season. This may call into question the predictions to date on summer drying made at GFDL and elsewhere. The runoff formulation underestimates runoff, leading to further overestimates of evaporation. (4) A finite-difference model for heat conduction in freezing and thawing soil has been developed and verified against analytic solutions. It may be used in the development of improved heat-storage algorithms for GCM land parameterizations.

WR064 ICE AND CLIMATE

TITLE: Ice and Climate

PROJECT NUMBER: WR 70-064

LOCATION: Arctic Ocean, Antarctica, Washington, Colorado, Wyoming, Utah

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, worldwide and regional, essentially are unknown. Two major technological advances 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) Acquire data to test the numerical models of the Arctic and Antarctic ice sheets and ice packs by directly participating in remote-sensing and surface-truth experiments and from remote-sensing polar-orbiting satellites. (2) Investigate the dynamics and thermodynamics of the upper ocean and their relation to the ice thickness, the results to be applied to the sea-ice-cover models (3) Investigate the use of satellite passive microwave data for snow-water equivalent mapping for various areas, including the Upper Colorado River Basin and China (4) Construct multidimensional time-dependent models of glacier flow and ice-sheet flow and test them with observations of glaciers.

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

PROGRESS: Directed the acquisition of the sequential aircraft synthetic-aperture radar images of the Barents Sea during the winter Seasonal Ice Zone Experiment (SIZEX) emulating the data flow from the ERS-1 satellite. Coordinated the acquisition of snow and ice surface properties with the USGS/NASA/ERIM in situ microwave instrument (SIDS) and the aircraft flights. This field program has yielded the most comprehensive data set of ice, ocean, and atmosphere observations of the winter Seasonal Ice Zone. Published a paper showing the decadal trends in sea ice extent and concentrations for both polar regions. The ice radar program completed selection of the Greenland ice core drill sites, GISP2, and completed the second of two field seasons of short-pulse ice radar studies in West Antarctica. Started processing of digital ice radar data. The joint USGS/NASA/USDA snow program continued with the in situ sequential measurement of snowpack properties at key locations in the Upper Colorado River Basin. The program has obtained SSM/I satellite observations to extend the satellite observational record to 10 years. Published papers showing the strong correlation of snow-water equivalent with brightness temperature. At South Cascade Glacier, the 2-decade-long program of mass balance data continues, and has shown record negative mass balance for the past 2 years. At Hubbard Glacier, in cooperation with the Alaska District Office, camera sites have been established and sequential oblique photography of the terminus region has been abtained, along with seasonal sequential vertical photography of the lower reach. The drastic retreat of Columbia Glacier continues to be monitored. The joint USGS/CNES program continued its satellite radar altimetric studies of the global ocean wave fields by processing and beginning the analysis of 2 years of Geosat data. As leaders of the snow and ice protocol with the People's Republic of China, carried out a field-site-inspection and data-exchange visit.

REPORTS PUBLISHED:

Gloersen, P., and Campbell, W.J., 1988, Satellite and aircraft passive microwave observations during the Marginal Ice Zone Experiment in 1984: Journal of Geophysical Research, v. 93, no. C6, p. 6837-6846.

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Krimmel, R.M., 1988, Terminus of Glaciar O'Higgins, southern Chile: Journal of Glaciology, v. 34, no. 116, p. 142.

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Krimmel, R.M., 1989, Mass balance and volume of South Cascade Glacier, Washington, 1958-1985, in Oerlemans, J., ed., Glacier fluctuations and climatic change: Kluwer Academic Publishers, p. 193-206.

Krimmel, R.M., and Meier, M.F., 1989, Glaciers and glaciology of Alaska: American Geophysical Union, 28th International Geological Congress, Field Trip Guidebook T301, 61 p.

Mognard, N.M., Campbell, W.J., and Josberger, E.G., 1988, Geosat surface wind speed estimates and comparisons in the North Atlantic for March 1987, in Chelton, D.B., ed., Appendix to U.S. WOCE Technical Report No. 2 WOCE/NASA Altimeter Algorithm Workshop, Oregon State University, Corvallis, Or., August 24-26, 1987, Proceedings.

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, p. 607-617.

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 freshwater, winds, and stratification due to salinity. The basin topography (bathymetry), air-water interaction, water-sedimentation interface, mixing characteristics, frictional loss at the bottom, and the rotational effects of the earth, together with the above-mentioned driving forces, constitute an extremely complicated balance that conserves mass, momentum, energy, and conservative solutes in the system.

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

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

PROGRESS: (1) The center of activity of the interagency study of San Francisco Bay/Delta has shifted to Sacramento; however, this project has continued to provide technical guidance and support to the interagency group. Jon Burau stayed on detail in this project. The project chief served as a technical advisor to overall modeling research, and Jeff Gartner provided technical advice and support to the field-data-collection program of the interagency San Francisco Bay study group. Additionally, the project has taken on the hydrodynamic tasks of the Division's Toxics program at Calcasieu River in Louisiana. Investigations are near completion, and a report of the study is being prepared. (2) Significant progress has been made in structuring a modeling system for estuarine hydrodynamic research. A bathymetry data base and a field-data archives system along with several models, have been integrated into a modeling system. A tidal circulation model of any subembayment of San Francisco Bay can now be implemented easily as needed. Several two-dimensional estuarine models have been calibrated and verified, and they are 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 expanding our research efforts to three-dimensional hydrodynamic modeling, to improve the accuracy of the models, and to consider simulations for long-term transport processes with these hydrodynamic models. (3) Because of the project's research contributions in shallow estuaries and bays, we were elected to host the 1988 biennial International Conference on Physics of Shallow Estuaries and Bays. We raised funds from National Science Foundation and convened the Conference, and the project chief chaired and directed the Conference,which took place November 29-December 2, 1988, in Asilomar, Calif. Forty papers were presented by leading researchers from 10 different countries. The project chief is now serving as the editor of a proceedings volume, and 33 full-length papers are currently being reviewed by colleagues around the world before publication. (4) Lastly, as an aside, the project has advocated the importance of using computer graphics for visualizaton of science. Efforts in this area are gaining recognition by other colleagues.

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Cheng, R.T., Wong, H.F.N. and Casulli, V., 1988, A multi-mode Eulerian-Lagrangian method for unsteady flows in a channel network [abs.], in Thirteenth International Conference on Mathematical Programming, Tokyo, Japan.

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Cheng, R.T., Feng, S., and Xi, P., 1989, On inter-tidal transport equation, in Neilson, Kuo, and Brubaker, eds. Estuarine circulation, Humana Press, p. 133-156.

Burau, J.R., and R.T. Cheng, 1989, A general method for generating bathymetric data for hydrodynamic computer models--Computer program documentation and application to San Francisco Bay, California, U.S. Geological Survey Open-File Report 89-28.

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 scientists and crew.

PROGRESS: Provided research-vessel support for several projects whose research is directed toward San Francisco Bay and other Pacific Coast estuarine systems. (See projects WR140 and WR164 for detailed progress statements.)

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 are the primary reservoir of ice on Earth, and they change in response to climate, flow instabilities, and geologic processes. Basic facts, such as whether the glacial ice volume in North America is increasing or decreasing, are generally unknown or disputed. Time-response characteristics of glaciers and effects on related natural systems are poorly understood. As a result, predictive models are usually only conceptual in nature. Direct observation of changes in behavior of glaciers by surveying, instrumentation, and aerial photography show that substantial and often unanticipated changes take place from year to year. Remote sensing has not been developed sufficiently to replace these observations.

OBJECTIVE: Understand mountain climate, behavior of glaciers , and related geologic and hydrologic processes of the current glaciation of North America. Determine whether glaciers are growing or shrinking, why these changes take place, rates of glacial response, and what effects can be anticipated. Detect and monitor significant glacial changes as they take place, whether or not they can be explained by current theory. Expand existing concepts and models and develop new explanations when the opportunity exists. Maintain continuity in this long-term research in which the Geological Survey has an established leadership role.

APPROACH: Develop unbroken observation sets at selected sites by operating long-term instrumentation year-around at selected glaciers with different controlling processes to document variations in mountain climate, glacial mass, glacial flow, and effects on related hydrologic systems. Publish the information and interpret findings about those processes that dominate different types of glacial behavior and their effects. Examine glacier-covered regions by reconnaissance air photography to discover and record significant changes from year to year.

PROGRESS: Three scientific papers and one abstract were published as a result of research conducted at Hubbard Glacier, which isolated Russell Fiord in 1986 and produced an outburst of 105,000 m^3/s peak discharge when the ice dam failed. The papers analyzed the glacier's geologic history, process of submarine glacial-moraine advance, reasons for ice-dam formation and failure, hydrology of the lake filling, and preliminary assessments of the possibility of continued glacial advance and its effects. One published abstract explained that Wolverine Glacier is continuing to growing because of increased snowfall and increased winter temperatures. Detailed analyses of unpublished glacial climate, mass-balance, and ice-flow data reports are being compiled for a set of data and interpretive reports.

REPORTS PUBLISHED:

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Mayo, L.R., in press, Advance of Hubbard Glacier and 1986 outburst of Russell Fiord, Alaska: Annals of Glaciology, v. 11.

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

OBJECTIVE: Understand the physical processes responsible for the transport of conservative and nonconservative solutes of physical, biological and chemical importance. Develop conceptual, statistical, and numerical models of these processes through the use of time-series analysis and other methods.

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

PROGRESS: Development of finite-element tidal and residual circulation models and a network generator has allowed a quantitative analysis of circulation in several estuaries and coastal seas. Interdisciplinary studies include an investigation of the variations in glacial mass balance in relation to large-scale climatic influences.

REPORTS PUBLISHED:

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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 can be influenced. The interactions are both physical and chemical and occur over a wide range of time periods and distances 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 that are consistent with the availability of parametric field information and field verification data to aid in the 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, sulfate retardation and attenuation can be identified with concurrent application of lithium transport simulations (Summit Co., Colorado; work with McKnight). In the acid mine drainage site, St. Kevin Gulch, an instream injection of lithium tracer is being used with the transient storage transport formulation to estimate instream physical parameters (Leadville, Colo. --Upper Arkansas River Toxic Substances Hydrology Site; work with Kimball and McKnight). Comparisons of multiple tracer injections and repeated stream gaging in Little Lost Man Creek have revealed that as much as 25 percent of the discharge may be through the intergravel zones of the channel (Orick, Calif.).

REPORTS PUBLISHED:

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

OBJECTIVE: Seek a full understanding of various fluvial processes on hillslopes and in river channels that undergo changes in response to rapid disturbances such as torrential storms, sudden snowmelt or glacier melt, dam break, volcanic eruptions, and earthquakes. Improve or generalize existing empirical formulas that do not accurately describe the process-response relationships. Develop new relations for various soils and highly concentrated sediment-water mixtures such as those posed in the form of rheological or constitutive equations. Build mathematical models, on the basis of such relations, for flash floods, debris flows, channel changes, and so forth. 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 than they are at present. Formulate rheological or constitutive equations for various soils and highly concentrated sediment-water mixtures, and determine the values of rheological parameters and material constants from available field or laboratory data. Build mathematical models for flash floods, debris flows, channel changes, and so forth, and solve them on digital computers by use of optimum numerical schemes. Verify the models against actual events.

PROGRESS: Debris-flow research has progressed in all theoretical, experimental, and field phases. Significant results obtained from tasks in the theoretical phase were the theoretical expressions of two-dimensional velocities and surface profiles for a steady nonuniform debris flow established in a flume with bed driven in the opposite direction of flow by a conveyor belt (that is, the "conveyor-belt" flume). These theoretical expressions resulted from the extension of the theory developed for unifom debris flow to that for nonuniform debris flow by means of the generalized viscoplastic fluid (GVF) model. The theoretical expressions of the slip velocity at the bed and the position of zero velocity normal to the bed in the flume were also derived. The derived relation between the slip velocity and the velocity gradient at the bed was found to be compatible with relations assumed by previous investigators. The accurate measurements of the slip velocity and the position of zero velocity normal to the bed, along with measurable free-surface velocity determined the rheological parameters of the GVF model. Data on these measurements constituted significant results from tasks in the experimental phase of debris-flow research. Two papers documenting these results were prepared. For the field phase of debris-flow research, the feasibility of investigating debris-flow hazards in Los Angeles County was explored. A United States Geological Survey interdivision research proposal on this investigation was prepared for the California District. Further accomplished was the preparation of two journal papers (one having been published and the other accepted), which address critical issues in modeling flow resistance on the basis of the power law.

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Chen, C.L., 1989, Power law of flow resistance in open channels--Manning's formula revisited in International Conference on Channel

Flow and Catchment Runoff Centennial of Manning's Formula and Kuichling's Rational Formula, University of Virginia, Charlottesville, Va., May 22-26, 1989, Proceedings: p. 817-848.

Chen, C.L., in press, Issues in debris flow research--personal views U.S., in Subitsky, Seymour, ed., Selected Papers in the Hydrologic Sciences: U.S. Geological Survey Water-Supply Paper 2340.

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 the modeling of transport of sediments, including mudflows and hyperconcentrations such as occur after natural disasters such as volcanic eruptions or dam failures.

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

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

PROGRESS: Completed coding and mathematical verification of a sediment-transport model that includes cotransport and reactions of sorbed constituents for bed material and wash load. Trial simulations were begun with field data from the Clark Fork River, Montana. Various mechanisms were investigated for simulating the observed exponential decay curve of the concentration of contaminated particles in bed sediments.

WR201 Hydroclimatic Uncertainty

TITLE: Resolution of Hydroclimatic Uncertainty

PROJECT NUMBER: WR 89-201

LOCATION: Topical Research

PROJECT CHIEF: Moss, Marshall E.

HEADQUARTERS OFFICE: Tucson, AZ

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

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

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

PROGRESS: A U.S. Geological Survey Circular was completed that describes the elements of and strategies for a research initiative on the hyrologic implications of climate uncertainty. From this Circular, the project and its approach were conceived and steps toward its initiation have been taken. No significant results have been obtained during the brief life of this project.

REPORTS PUBLISHED:

Moss, M.E. and Lins, H.F.,1989, Water resources in the twenty-first century--a study of the implications of climate uncertainty: U.S. Geological Survey Circular 1030, 25 p.

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

NORTHEASTERN REGION

PROJECT NUMBER	PROJECT SHORT TITLE	PAGE
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WR012	Limnology: Benthic Communities	23
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WR046	Geochem Rivers and Estuaries	25
WR064	Ice and Climate	280
WR065	Solute Partitioning	120
WR068	Organic Chemicals in Subsurface	27
WR076	Chemistry Of Hydrosolic Metals	252
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WR102	Modeling Geothermal Systems	173
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WR121	Heat and Mass Transport--Cascades	176
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WR127	Energy Transport in Ground Water	179
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WR137	Toxic Substances: Aquatic Ecosystems	32
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WR140	Hydrodynamics of Tidal Estuaries	283
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WR174	Microbial Biogeochemistry	40
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WR187	Flow and Geochemical Interactions	292
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