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WATER RESOURCES DIVISION,

U.S. GEOLOGICAL SURVEY,

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Compiled by Martha L. Nichols and Linda C. Friedman

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CONTENTS

Page

INTRODUCTION 1

ECOLOGY 5

CR 84—286 Interactions Between Organic Solutes and Trace Metals in Natural Waters, and Their Ecological Role 6
PROJECT CHIEF: McKnight, Diane M.

CR 85—293 The Role of Chemical Fluxes in the Biogeochemistry of Inland Surface Waters, Including Lakes, Reservoirs, and Wetlands 10
PROJECT CHIEF: LaBaugh, James W.

CR 86—295 Microbial Transformation of Dissolved Organic Carbon in Aquatic Environments 12
PROJECT CHIEF: Smith, Richard L.

CR 88—312 Ecological Interactions of Lakes and Streams 15
PROJECT CHIEF: Averett, Robert C.

CR 91—320 Characterization of Biotic and Biogeochemical Interactions at Environmental Interfaces 17
PROJECT CHIEF: Striegl, Robert G.

CR 90—323 Interdisciplinary Research Initiative at the Shingobee Headwaters Research Area, Minnesota 19
PROJECT CHIEF: Winter, Thomas C. and Averett, Robert C.

NR 73—090 Remote Sensing and Ecological Research in Wetlands 21
PROJECT CHIEF: Carter, Virginia P.

NR 87—136 Modeling of Microbially Catalyzed Geochemical Reactions in Aquatic Environments 24
PROJECT CHIEF: Lovley, Derek R.

NR 90—145 Vegetation and Hydrogeomorphic Relations 27
PROJECT CHIEF: Hupp, Cliff R.

WR 61—012 Limnology: Controls on Distribution and Composition of Benthic Communities of Inland Aquatic Ecosystems 29
PROJECT CHIEF: Slack, Keith V.

WR 68—046 Geochemistry of Riverine and Estuarine Waters 31
PROJECT CHIEF: Peterson, David H.

WR 71—068 Fate of Organic Chemicals in Subsurface Environments 34
PROJECT CHIEF: Godsy, Edward M.

WR 75—125 Availability of Trace Elements in Sediments to Aquatic Organisms 36
PROJECT CHIEF: Luoma, Samuel N.

WR 75—137 Effects of Toxic Substances on Aquatic Communities 39
PROJECT CHIEF: Leland, Harry V.

WR 76—145 Biotic Response to Climatic Variability and Human Impacts in arid lands 41
PROJECT CHIEF: Betancourt, Julio

WR 79—164 Plankton Dynamics in Tidal Estuaries 45
PROJECT CHIEF: Cloern, James E.

WR 81—174 Microbial Biogeochemistry of Aquatic Environments 48
PROJECT CHIEF: Oremland, Ronald S.

WR 84—186 Biotic Interface with Fluvial Transport: Processes Associated with Dissolved Solutes in Transport 51
PROJECT CHIEF: Triska, Frank J.

WR 86—190 Solute Transport Involving Biological Processes in Surface Waters 54
PROJECT CHIEF: Kuwabara, James S.

WR 86—191 Interaction of Bacteria with Environmental Contaminants and Solid Surfaces in the Aquatic Environment 57
PROJECT CHIEF: Harvey, Ronald W.

WR 86—192 Environmental Influences on Estuarine Benthic Community Dynamics 60
PROJECT CHIEF: Nichols, Frederic H.

GEOMORPHOLOGY AND SEDIMENT 63

CR 75—102 Movement and Storage of Sediment in River Systems 64
PROJECT CHIEF: Meade, Robert H.

CR 65—105 Effects of Water and Sediment Discharges on Channel Morphology 66
PROJECT CHIEF: Williams, Garnett P.

CR 74—187 Hydraulics and Mechanics of Bedload—Transport Processes 68
PROJECT CHIEF: Emmett, William W.

CR 81—266 Transport and Deposition of Sediments and Sediment—Borne Contaminants in Tidal Rivers and Estuaries 71
PROJECT CHIEF: Glenn, Jerry L.

CR 82—273 River Mechanics 73
PROJECT CHIEF: Andrews, Edmund D.

CR 87—309 Sediment—Transported Pollutants in the Mississippi River 76
PROJECT CHIEF: Meade, Robert H.

CR 79–311 Sediment Impacts from Disturbed and Undisturbed Lands 78
PROJECT CHIEF: Osterkamp, Waite R.

CR 88–313 Sediment–Water Chemistry in Large River Systems:
Biogeochemical, Geomorphic, and Human Controls 81
PROJECT CHIEF: Stallard, Robert F.

WR 89–200 Response of Fluvial Systems to Climatic Variability 84
PROJECT CHIEF: Webb, Robert H.

GROUND-WATER CHEMISTRY 87

CR 77–223 Transuranium Research 88
PROJECT CHIEF: Cleveland, Jesse M.

CR 82–276 Geochemistry of Clay-Water Reactions 90
PROJECT CHIEF: Eberl, Dennis D.

CR 83–283 Environmental Dynamics of Persistent Organic Compounds 93
PROJECT CHIEF: Chiou, Cary T.

CR 89–318 Reaction-Transport Modeling in Ground-Water systems 96
PROJECT CHIEF: Parkhurst, David L.

NR 69–020 Mineral-Water Interaction in Saline Environments 98
PROJECT CHIEF: Jones, Blair F.

NR 57–034 Spatial Distribution of Chemical Constituents in Ground Water 101
PROJECT CHIEF: Back, William

NR 74–041 Interface of Paleoclimatology and Aquifer Geochemistry 104
PROJECT CHIEF: Winograd, Isaac J.

NR 76–056 Kinetics and Thermodynamics of Chemical Evolution in
Ground-Water Systems 106
PROJECT CHIEF: Plummer, L. Niel

NR 75–064 Physical Chemistry of Stable Isotope Fractionation in
Hydrologic Processes 110
PROJECT CHIEF: Coplen, Tyler B.

NR 79-093 Chemical Models of Natural Systems 113
PROJECT CHIEF: Thorstenson, Donald C.

NR 81–122 Dispersion of Toxic and Radioactive Wastes in
Ground-Water Systems 115
PROJECT CHIEF: Wood, Warren W.

NR 83–129 Comparative Study of Organic Degradation in Selected
Hydrogeologic Environments 117
PROJECT CHIEF: Baedecker, Mary Jo

NR 79—132 Relationship Between Chemical Quality of Natural Waters and Human Health and Disease 119
PROJECT CHIEF: Feder, Gerald L.

NR 82—138 Uranium-Thorium Series Radioisotopes in Ground-Water and Surface-Water Systems 121
PROJECT CHIEF: Kraemer, Thomas F.

WR 68—036 Factors Determining Solute Transfer in the Unsaturated Zone 123
PROJECT CHIEF: James, Ronald V.

WR 70—065 Partitioning of Solutes between Solid and Aqueous Phases 125
PROJECT CHIEF: Davis, James A., III

WR 91—080 Stable Isotope Tracers of Biogeochemical and Hydrologic Proces 128
PROJECT CHIEF: Kendall, Carol

WR 75—128 Chemical Modeling and Thermodynamic Data Evaluation of Major and Trace Elements in Acid Mine Waters and Ground Waters 131
PROJECT CHIEF: Nordstrom, Darrell K.

WR 76—139 Geochemistry of Water in Fine Grained Sediments 134
PROJECT CHIEF: Kharaka, Yousif K.

WR 79—165 Chemical and Isotope Studies of Thermal Waters of the Western United States 137
PROJECT CHIEF: Mariner, Robert H.

WR 84—189 Chemistry of Aquatic Organic Matter 140
PROJECT CHIEF: Goerlitz, Donald F.

WR 88—196 Geochemical Reactions Between Water and Mineral Substrates 143
PROJECT CHIEF: White, Arthur F.

GROUND-WATER HYDROLOGY 147

CR 74—090 The Role of Lakes in the Hydrologic System, with Emphasis on Their Relation to Ground Water 148
PROJECT CHIEF: Winter, Thomas C.

CR 64—140 Borehole Geophysics as Applied to Geohydrology 150
PROJECT CHIEF: Paillet, Frederick L.

CR 76—191 Mathematical Simulation of Subsurface-Water Flow Using Uncertain and Incomplete Data 154
PROJECT CHIEF: Cooley, Richard L.

CR 69—200 Field Applications of Unsaturated Zone Flow Theory 156
PROJECT CHIEF: Weeks, Edwin P.

CR 85—292 Ground-Water Solute-Transport Simulation 159
PROJECT CHIEF: Kipp, Kenneth L.

CR 90—319 Application of Stochastic Processes in Hydrogeology 162
PROJECT CHIEF: Naff, Richard L.

NR 81—035 Hydrologic Behavior of Cretaceous Shales 164
PROJECT CHIEF: Neuzil, Christopher E.

NR 78—089 Investigations of Single and Multiphase Fluid Flow, Mass and Energy Transport, and Fluid Phase Change in the Subsurface Environment 166
PROJECT CHIEF: Voss, Clifford I.

NR 81—120 Digital Modeling of Transport in the Saturated Zone 168
PROJECT CHIEF: Konikow, Leonard F.

NR 84—130 Multivariate Statistical Techniques for Assessing Regional Ground—Water Quality and Quantity 171
PROJECT CHIEF: Brown, Charles E.

NR 84—134 Transport Phenomena in Fractured Rock 173
PROJECT CHIEF: Shapiro, Allen M.

NR 73—139 The Mathematical Simulation of the Transport and Reaction of Chemical Species in Ground Water 175
PROJECT CHIEF: Grove, David B.

WR 63—024 Application of the Unsaturated Flow Theory to the Phenomena of Infiltration and Drainage 176
PROJECT CHIEF: Stonestrom, David A.

WR 73—102 Modeling and Monitoring Heat and Fluid Flow in Geothermal Systems 178
PROJECT CHIEF: Sorey, Michael L.

WR 72—108 Technical Coordination and Support of WRD Geothermal Studies 180
PROJECT CHIEF: Sorey, Michael L.

WR 74—121 Hydrologic Studies of Heat and Mass Transport 181
PROJECT CHIEF: Ingebritsen, Steven E.

WR 75—127 Analytical Modeling of Flow and Transport in Aquifers and Geothermal Reservoirs.................................. 184
PROJECT CHIEF: Moench, Allen F.

WR 76—171 Hydrologic Analysis of Petrofabrics--Sandstones 186
PROJECT CHIEF: Getzen, Rufus T.

WR 75—176 Water Wells as Strain Meters 187
PROJECT CHIEF: Bredehoeft, John D.

WR 82—178 Models for Ground-Water Management 189
PROJECT CHIEF: Gorelick, Steven M.

WR 82–179 Nonisothermal Multiphase Flow 191
PROJECT CHIEF: Herkelrath, William N.

WR 82–180 Theories of Water Flow and of Solute Transport in the Unsaturated Zone 193
PROJECT CHIEF: Rubin, Jacob

WR 83–184 Hydrology of Fractured Rocks 195
PROJECT CHIEF: Hsieh, Paul A.

WR 87–193 Temperature Effects in the Unsaturated Zone 197
PROJECT CHIEF: Constantz, James E.

WR 89–198 Physical Characteristics that Determine Flow in the Unsaturated Zone 199
PROJECT CHIEF: Nimmo, John R.

WR 89–199 The Fate and Transport of Immiscible Contaminants in the Subsurface 201
PROJECT CHIEF: Essaid, Hedeff I.

SURFACE-WATER CHEMISTRY 203

CR 68–046 Origin, Characterization, and Quantification of Natural Organic Solutes in Water 204
PROJECT CHIEF: Malcolm, Ronald L.

CR 68–132 Behavior of Natural Polyelectrolytes in Water 207
PROJECT CHIEF: Wershaw, Robert L.

CR 75–189 Geochemical Kinetics Studies of Silicate Rock Hydrologic Systems 211
PROJECT CHIEF: Claassen, Hans C.

CR 76–199 Water Chemistry of Sediment Surface Coatings 213
PROJECT CHIEF: Goldberg, Marvin C.

CR 82–207 Arid Regions Climate and Chemistry 217
PROJECT CHIEF: Benson, Larry V.

CR 83–282 Research in Analytical Environmental Trace Element Chemistry and Its Impact on Water Quality 220
PROJECT CHIEF: Taylor, Howard E.

CR 83–284 Corrosion of Building Materials as Determined From Solid Weathering Products Removed by Wet Precipitation 223
PROJECT CHIEF: Reddy, Michael M.

CR 84–285 Comprehensive Organic Analysis of Water 226
PROJECT CHIEF: Leenheer, Jerry A.

CR 89–316 Solid Phase Chemistry and Related Environmental Processes 230
PROJECT CHIEF: Seeley, James

NR 76—065 Sedimentary Geochemical Processes Affecting the Exchange of Nutrients and Transition Metals Between Sediment and Water in Riverine, Estuarine, and Lacustrine Environments 232
PROJECT CHIEF: Callender, Edward

NR 78—092 Hydrogeochemical Controls on the Migration of Radionuclides from Uranium Mill Tailings 235
PROJECT CHIEF: Landa, Edward R.

NR 79—099 Carbon Fluxes in Hydrologic and Geologic Processes 237
PROJECT CHIEF: Sundquist, Eric T.

NR 81—109 Geochemical Cycling of Trace Elements and Nutrients in Natural Water Systems 239
PROJECT CHIEF: Bricker, Owen P.

NR 86—135 Distribution and Speciation of Metals in Sedimentary Environments 242
PROJECT CHIEF: Simon, Nancy S.

WR 57—076 Chemistry of Hydrosolic Metals and Related Constituents of Natural Water 245
PROJECT CHIEF: Hem, John D.

WR 83—204 Origin, Fate, and Transport of Organic Compounds in Surface and Ground Waters and Their Effect on Water Quality 248
PROJECT CHIEF: Pereira, Wilfred E.

SURFACE-WATER HYDROLOGY 251

CR 77—228 Precipitation-Runoff Modeling of Watershed System 252
PROJECT CHIEF: Leavesley, George H.

CR 83—279 Statistical Analysis of Errors in Hydrologic Models 255
PROJECT CHIEF: Troutman, Brent M.

CR 77—301 Transport and Degradation of Organic Substances in Streams 258
PROJECT CHIEF: Rathbun, Ronald E.

CR 90—321 Paleohydrology and Climate Change 261
PROJECT CHIEF: Jarrett, Robert

NR 69—019 Numerical Simulation of Hydrodynamic Processes in Rivers, Estuaries, and Coastal Embayments 263
PROJECT CHIEF: Baltzer, Robert A.

NR 79-096 Computational Hydraulics for Surface Water Problems 266
PROJECT CHIEF: Lai, Vincent C.

NR 80—104 Simulation Modeling of Hydrodynamic Systems 268
PROJECT CHIEF: Schaffranek, Raymond W.

NR 82—125 Hydrologic Regression and Data-Network Design in Coal Mining Regions ... 271
PROJECT CHIEF: Tasker, Gary D.

NR 84-133 Regional Hydrologic Processes ... 274
PROJECT CHIEF: Landwehr, Jurate M.

NR 88—143 Research Vessel Leopold Operations in Potomac River, Chesapeake Bay, and Adjacent Coastal Waters ... 276
PROJECT CHIEF: Grove, David B.

NR 88—144 Continental Hydrology and Global Climate ... 277
PROJECT CHIEF: Milly, Chris D.

NR 90—147 Transport of Dissolved and Suspended Materials in Surface Waters ... 279
PROJECT CHIEF: Lee, Jonathan

NR 90—148 Regional Water-Quality Assessment ... 281
PROJECT CHIEF: Alley, William

WR 70—064 Ice and Climate ... 283
PROJECT CHIEF: Campbell, W.J.

WR 76—140 Hydrodynamics and Mathematical Modeling of Circulation and Transport Phenomena in Tidal Estuaries ... 287
PROJECT CHIEF: Cheng, Ralph T.

WR 77—156 Research Vessel Polaris Operations in San Francisco Bay and Adjacent Coastal Ocean ... 290
PROJECT CHIEF: Conomos, T. John

WR 83—183 Analysis and Modeling of Conservative and Nonconservative Transport Processes ... 291
PROJECT CHIEF: Walters, Roy A.

WR 84—187 Coupled Transport and Geochemical Processes Determining the Fate of Chemicals in Surface Waters ... 293
PROJECT CHIEF: Bencala, Kenneth E.

WR 83—194 Fluvial Processes and River Mechanics ... 296
PROJECT CHIEF: Chen, Cheng-lung

WR 73—197 Mathematical Modeling Principles ... 298
PROJECT CHIEF: Bennett, James P.

WR 89—201 Resolution of Hydroclimatic Uncertainty ... 299
PROJECT CHIEF: Moss, Marshall E.

APPENDIX.--Alphabetical listing by Project Chief ... 301

THE NATIONAL RESEARCH PROGRAM OF THE WATER RESOURCES DIVISION, U.S. GEOLOGICAL SURVEY FISCAL YEAR 1991

Compiled by Martha L. Nichols and Linda C. Friedman

INTRODUCTION

The National Research Program (NRP) has been an integral part of the of the U.S. Geological Survey's Water Resources Division (WRD) since the late 1950's. Since that time, the NRP has grown to include the study of a broad spectrum of scientific problems related to water resources. The research encompasses aspects of many fields (hydrology, geology, chemistry, physics, ecology, biology, mathematics, and engineering) to gain a fundamental understanding of the processes that affect the availability, movement, and quality of the Nation's water resources. In addition to developing improved understanding of hydrologic processes, the knowledge gained through NRP research are important to all other aspects of WRD's programs. The NRP works to identify new issues, develop and test new techniques of investigation, train scientists throughout the Division, and advise program managers on scientific issues.

The NRP is defined by four principal characteristics:

1. The purpose of the program is to acquire new hydrologic knowledge of general significance, especially knowledge that involves new hydrologic principles and broadly applicable hydrologic methods.

2. The program is reasonably comprehensive in the sense that all of the key subdisciplines of hydrology are represented, and the management of the program is strongly based within these subdisciplines through the use of a system of research advisors who guide the development of the program.

3. A major proportion of the scientific staff of the NRP are specialists, whose scientific achievements are widely known and respected by their peers. The program also develops junior scientists who have the background for, and aspire to, such scientific recognition. The existence of such a staff of specialists, pursuing research goals with long-term continuity, is necessary to provide the WRD, the U.S. Geological Survey (USGS), and indeed the whole Federal Government with the necessary expertise to begin to understand new, poorly understood hydrologic problems as they arise.

4. The scientists within the NRP are clustered in a few locations, each with a variety of subdisciplines. This is done to achieve a critical mass of scientific expertise that generates creative new ideas and approaches as a result of frequent interaction of scientists from a variety of different disciplines. Because of the size of these groups (around 100 people including support staff) at each location, there is an opportunity for many scientific collaborations that would be quite difficult if the scientists were isolated in small groups.

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 guidance, 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*—Concerned with 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*—Concerned with 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, studies are underway 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 1991. 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 1991. Because of the long-term nature of the program, the bibliographic information provided covers a 5-year period. It does not include abstracts or informal reports. Rather it contains those reports that are readily available in the form of journal articles, USGS publications, book chapters, or books.

This report is intended to describe the work in progress, the expertise, and most importantly the publications produced by the NRP. Readers are encouraged to seek copies of these publications from the specific NRP project that prepared them. Addresses and phone numbers of Project Chiefs are provided in the text. For the reader's convenience, an appendix provides an alphabetic list of the Project Chiefs of all projects included in this volume, the project's title, and page number of the project summary.

ECOLOGY

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

PROJECT NUMBER: CR 84—286

PROJECT CHIEF: McKnight, Diane M.

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

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

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

PROGRESS: An intensive study of Antarctic desert streams was carried out during the 1990/91 field season. Continuous records for streamflow, conductivity and temperature were carried out for eight of the major streams in the Lake Fryxell Valley during the period of flow. Parshall flumes were used at four of the streams. Major ions, dissolved organic carbon and nutrients were analyzed at 3-4 day intervals. These data are being analyzed in conjunction with temperature and solar radiation to understand climatic relationships. The geochemical results indicate that weathering reactions in the substream (hyporheic) zone are an important source of solutes to the streams. Investigations of Lake Fryxell water column iron profiles were also conducted to augment understanding of the chemical, hydrologic, and biological factors that influence iron cycling in permanently anoxic basins. Measurements of concentration and speciation of particulate, colloidal and dissolved forms reveal strong redox-mediated transformations and suggest that biologically mediated reactions are active in the photic zone. Analysis of phytoplankton species and productivity at Lake Fryxell showed that the extreme stability of the water column and chemical gradients resulted in depthwise variations in species distribution. For example, filamentous blue-green algae are consistently found just above the oxycline but chrysophyte abundance is highly variable. A study of winter (under ice) phytoplankton in Loch Vale (Colorado Water Energy and Biogeochemical Budgets (WEBB) site) was completed. Phytoplankton species abundance varied with clarity of the ice cover during the winter.

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

PROJECT NUMBER: CR 85–293

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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: A report was written on the interrelation of changing hydrological conditions, chemical characteristics, and wetland vegetation at my Cottonwood Lake area, North Dakota study site for the period 1967-89, with emphasis on the period of detailed study, 1979–89. This has been submitted for publication in the definitive international summary of research on aquatic ecosystems in semiarid regions. Intensive studies of chemical fluxes, including determination of ground water flux and in lake chemical and biological investigations, continued at Cottonwood Lake area wetlands, North Dakota, Crescent Lake National Wildlife Refuge, Nebr., and Shingobee and Williams Lakes, Minn.

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ECOLOGY

TITLE: Microbial Transformation of Dissolved Organic Carbon in Aquatic Environments

PROJECT NUMBER: CR 86—295

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

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

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

PROGRESS: (1) Micro-organisms that have been genetically engineered (GEMs) to degrade specific organic compounds are often proposed as mechanisms for bioremediation of contaminated groundwater. One such GEM is a strain of Pseudomonas B13 which has been engineered to degrade chlorinated aromatic hydrocarbons. However, little is known about the survival and the ability of such organisms to function within the context of a groundwater contaminant plume. Therefore, an in situ survival experiment was undertaken in which the nonengineered, parent strain of Pseudomonas B13 was injected into several zones of an aquifer that had been contaminated with sewage effluent. Viability within aquifer cores collected from the injection site was monitored by using conventional plating techniques and by using a gene probe specific for the organism. The test is still in progress. Currently, the organism has survived for more than 6 months in both oxic and anoxic portions of the contaminant plume, but survived less than 10 weeks in an uncontaminated zone of the aquifer. (2)

ECOLOGY

Denitrification (microbial reduction of nitrate to nitrogen gas) occurs in nitrate-contaminated groundwater, but is predominantly electron-donor limited. The addition of hydrogen to groundwater samples collected from a sewage contamination plume located in Massachusetts stimulated denitrification to the extent that more than 1 mM nitrate was consumed within 48 hours. These results demonstrated that denitrification could be manipulated via hydrogen stimulation to serve as a mechanism for bioremediation of nitrate contamination. Several strains of autotrophic, hydrogen-oxidizing, denitrifying bacteria were isolated from this aquifer and subsequently characterized. These organisms represented several different genera of bacteria, all could grow heterotrophically with oxygen or nitrate, and all could also use hydrogen aerobically. It appears that hydrogen-oxidizing denitrifying bacteria are commonly found in the subsurface. (3) A small-scale (10 m), natural gradient, tracer test was used to measure denitrification in situ in a nitrate-contaminated groundwater. This tests, which was originally developed to measure hydrologic properties of an aquifer, had been modified to measure microbial processes, such as denitrification. The results of this experiment are being simulated with a modified groundwater transport model to distinguish the action of microorganisms from the effect of advection and dispersion upon the tracer cloud and to determine the Michaelis Menten kinetic parameters for the denitrification process. It appears that more conventional activity measurements using core material collected from the aquifer with a drilling rig may over-estimate the rate of the activity in the subsurface. (4) Methane geochemistry was characterized in a permanently ice-covered, amictic lake in Antarctica in which the carbon cycle was dominated by internal processes. Methane was produced only within the sediments of the lake, entering the anoxic water column by diffusive flux, where it was entirely oxidized to carbon dioxide by anoxic microbial processes. Methane flux represented a significant fraction of the total carbon exchanging between the water column and the sediments, yet little isotopic fractionation was evident for the methane carbon.

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TITLE: Ecological Interactions of Lakes and Streams

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

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

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

PROGRESS: Work continues on Williams and Shingobee Lakes. We have continued our work on stream habitats in Yellowstone National Park and in the Catskill Mountain streams of New York. This will be our last year (1992) of sampling these streams. All samples are sorted and many have been identified. The Grand Canyon study has started and two synoptic experiments have been completed as of June 1991.

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TITLE: Characterization of Biotic and Biogeochemical Interactions at Environmental Interfaces

PROJECT NUMBER: CR 91–320

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PROBLEM: Environmental interfaces are transitional zones where interactions between contacting systems occur. These interactions commonly result in hydrologic or chemical fluxes. Organisms may create the fluxes, as with gaseous fluxes across land-air and water-air interfaces created by metabolic processes; or they may associate with favorable conditions created by the fluxes, as with the association of some aquatic life forms with ground-water seeps in lakes. Change in the physical and chemical conditions that maintain biotic and biogeochemical interactions at interfaces can have extensive environmental effects. Evaluation of these effects requires an understanding of processes that control the natural condition.

OBJECTIVE: Characterize hydrologic and chemical fluxes that naturally occur across environmental interfaces; isolate biotic or biogeochemical causes of, or associations with, those fluxes; and, where possible, evaluate the effects of environmental change on the observed interactions. Develop process based models that explain field and laboratory observations.

APPROACH: Select appropriate field sites to characterize flux-associated interactions and systematically measure relevant variables. Conduct field and laboratory experiments to verify hypothesized interactions. Specific approaches are study dependent. Current field investigations are focused on characterization of methane and carbon dioxide fluxes at land-air and water-air interfaces, and on evaluation of the responses of macrobiota to ground-water fluxes in lakes.

PROGRESS: Field studies of methane and carbon dioxide exchange in alpine soils, desert soils, and tall grass prairie have been completed. Preliminary results were presented at the 1990 Fall American Geophysical Union (AGU) meeting, the 1991 Front Range AGU meeting, the 10th International Symposium on Global 27 Biogeochemistry, and the North Atlantic Treaty Organization (NATO) Advanced Research Workshop on the Global Methane Cycle. A model for methane transport and reaction that calculates net methane exchange with the atmosphere, and total methane consumption in unsaturated soils has been developed; a publication of that model, with application to the field studies is in progress.

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TITLE: Interdisciplinary Research Initiative at the Shingobee Headwaters Research Area, Minnesota

PROJECT NUMBER: CR 90—323

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PROBLEM: Many advances in hydrologic research are limited by the lack of communication between specialists in the large number of disciplines involved in studying the hydrologic system. For example, nearly all specialists need to make assumptions or estimates about hydrologic processes or fluxes that interface with the component of the hydrologic system they are dealing with. Therefore, interdisciplinary research needs to be focused on the interfaces between hydrologic components, hydrologic processes, and hydrologic landscapes in order to understand important interactions within the hydrologic system.

OBJECTIVE: This project is designed to facilitate interdisciplinary research by focusing a number of research projects on the physical, chemical, and biological aspects of the hydrologic system at specified field sites within the Shingobee Headwaters area in northern Minnesota. These field sites were selected to emphasize the interactions between the hydrologic components of atmospheric water, surface water, and ground water. By focusing a broad research approach at common localities in the landscape it is expected that significant advances can be made in understanding and modeling some of the important interactions within the hydrologic system.

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

PROGRESS: Surface-water gaging structures were installed on streams. A climate station was established to collect data on solar radiation, air temperature, wind speed and wind direction, and humidity. Wells and piezometers were constructed. Water samples were collected for chemical analysis.

TITLE: Remote Sensing and Ecological Research in Wetlands

PROJECT NUMBER: NR 73-090

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PROBLEM: Wetlands are hydrologically controlled ecosystems essential to estuarine, marine, lacustrine, and riverine productivity. To improve our understanding of these ecosystems we need information on (1) wetland hydrologic variables/budgets and their relation to wetland vegetation and nutrient cycling; (2) wetland dynamics and boundary fluctuations; (3) wetland functions and values; and (4) short- and long-term temporal changes. Wetland plants may serve as sensitive hydrologic indicators of water-quality parameters such as salinity, turbidity, pH, nutrients; presence of various pollutants; or frequency and duration of inundation.

Submersed aquatic wetlands have many functional values including (1) habitat for invertebrate species; (2) food and (or) shelter for juvenile and adult fish, waterfowl, and other wildlife; (3) retarding flow velocities, stabilizing bottom sediments, and slowing erosion; and (4) oxygenating the water, recycling nutrients and heavy metals. Decline or disappearance of aquatic plant communities or overgrowth of submersed vegetation under nutrient-enriched conditions is of concern to scientists, ecologists, environmentalists and managers. The factors affecting distribution and abundance of submersed aquatic vegetation and the effect of submersed aquatic vegetation on water quality are poorly understood.

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

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

PROGRESS: During 1990, we conducted an interdisciplinary velocity study in a dense *Hydrilla verticillata* bed in the tidal Potomac River in cooperation with the Numerical Simulation of Riverine and Estuarine Hydrodynamic Processes Project. The study showed that water velocities in the plant bed were very low compared with those in the channel. The direction of flow and movement of water in the bed are controlled by the head (water level) relation between the channel and bed water and by the distribution of plant biomass in the water column over the tidal cycle. Velocities and current directions on the unvegetated shoal (January) were generally similar to those in the channel. The results confirmed the results of earlier dye studies.

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

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TITLE: Modeling of Microbially Catalyzed Geochemical Reactions in Aquatic Environments

PROJECT NUMBER: NR 87—136

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

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

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

PROGRESS: It was discovered that respiratory Fe(III)-reducing micro-organisms can also use the oxidized form of uranium, U(VI), as an electron acceptor. The organisms can obtain energy for growth by oxidizing organic compounds or hydrogen with the reduction of U(VI) to U(IV). Previous geochemical dogma stated that the reduction of U(VI) in sedimentary environments was a strictly chemical reaction in which reduced compounds such as sulfide, hydrogen, or organic matter nonenzymatically reacted with U(VI) to reduce it. Studies in defined laboratory systems as well as with natural populations of micro-organisms living in sediments demonstrated that enzymatic reduction of U(VI) is a much more likely mechanism than chemical reactions to explain U(VI) reduction in sedimentary environments. Our studies have indicated that microbial U(VI) reduction is a likely explanation for important geochemical phenomena as: (1) the removal of dissolved uranium from aquatic environments by bottom sediments; (2) the formation of some types of uranium ore deposits; and (3) the accumulation of uranium in reduction spots. Furthermore, microbial reduction of uranium holds promise as an effective method for removing uranium from contaminated waters. It was discovered that micro-organisms in a wide variety of anaerobic aquatic sediments can consume chlorofluorocarbon (CFC) or freon. The freons have been implicated in the depletion of stratospheric ozone and are important greenhouse gases. CFC—11 and CFC—12 were previously considered to be biochemically inert. However, we demonstrated through a variety of experimental treatments with sediments that uptake was due to the activity of micro-organisms. Furthermore, we also demonstrated CFC uptake in a pure culture of an anaerobic micro-organism. The global significance of this previously unrecognized sink for CFC—11 and CFC—12 is yet to be determined. However, shallow aquatic environments in close proximity to the atmosphere are globally widespread and are already known to greatly affect the global methane cycle. Because of the long atmospheric lifetimes of CFC—11 and CFC—12, a sink that removes even a small fraction of the global CFC—11 and CFC—12 annually can have an important long-term effect on the extent of ozone depletion.

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TITLE: Vegetation and Hydrogeomorphic Relations

PROJECT NUMBER: NR 90—145

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PROBLEM: Many hydrogeomorphic processes are poorly understood. Ecologic and paleohydrologic (botanical evidence) studies will allow for improved flood (or debris flow) prediction for streams with short or no gaging-station records. Improvement of our understanding of the relation among fluvial geomorphology, sedimentation, mass wasting, plant chemistry, and plant ecology will provide insight into such problems as assessment of water quality, wetland reduction, long-term effects of climatic variation, and the frequency and magnitude of destructive hydrogeomorphic phenomena. Basic interdisciplinary research has only began in most basins studies; plant ecologic and geomorphic analyses may provide substantial information about variable source areas of runoff production and ground-water recharge.

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

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

ECOLOGY

PROGRESS: Hupp has initiated a pilot study, in cooperation with the University of North Carolina, along the Cape Fear Estuary to document and interpret the spatial and temporal patterns of saltwater encroachment and global sea-level rise using element analyses of wood tissue from cypress trees growing along a saline gradient. Initial results suggest that the analysis for chlorine bonded in tree rings will provide spatial and temporal details of salt-water encroachment along the southern Atlantic and gulf coasts heretofore unavailable. These results should allow for the development of predictive models that will be extremely useful in long-term planning in these areas. A continuing study, began last year, along the Chickahominy River, Va., has shown that riverine wetlands can remove more that 60 percent of the suspended sediments and nonpoint source pollutants (heavy metals, nutrients, organic compounds) between the headwaters near Richmond, Va., and the reservoir for Newport News, Va., a reach about 42 river-miles long. Additionally, Yanosky's work on heavy metal analysis in wood tissue has shown that the volume and timing of transport of these pollutants may be accurately estimated. This research project is still in its early phases, however, in cooperation with the Virginia office and at least two other NRP projects, we feel confident that over the next few years our efforts will yield important insight and information on the sediment/pollutant trapping nature of riverine wetlands, their biogeochemical budgets, and the greater role wetlands in water-quality maintenance. In cooperation with the Tennessee District and the U.S. Environmental Protection Agency (EPA), our project was able to document and determine the location and timing of off-site movement of ground-water contamination from a creosote production site (an EPA superfund project) through the element analysis of wood. Also in Tennessee, a dendrogeomorphic investigation, now mostly completed (except for writing journal articles) has shown that channelization exerts a stronger control on forested wetlands sedimentation that bridge construction or most agricultural activity. This research has led to considerable insight on the poorly understood temporal and spatial patterns of sediment deposition in wetlands, wetland hydrology and its effects on wetland-forest ecology; dendrogeomorphic techniques provide information heretofore unavailable. We are involved in several other smaller or beginning projects in Virginia, Maryland, Colorado, Minnesota (IRI), South Carolina, Rhode Island, and Louisiana concerned with wetlands and (or) fluvial geomorphology and vegetation process and form using dendrogeomorphic, plant ecologic, and trace element analyses.

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

PROJECT NUMBER: WR 61—012

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

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

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

PROGRESS: Project chief retired in 1990, but continues working part time to complete reports on invertebrate drift related to water quality.

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ECOLOGY

TITLE: Geochemistry of Riverine and Estuarine Waters

PROJECT NUMBER: WR 68-046

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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 climate related), long-term trends (human factors), and seasonal and short-term source-sink processes (photosynthesis/mineralization).

PROGRESS: Winter atmospheric circulation largely determines whether a year is wet or dry, controls the (high or low) amplitude of fresh water flows to San Francisco Bay estuary, and, thus, determines the salinity response. Spring atmospheric circulation, however, influences the timing of the fresh water flows, with early snow-melt driven flows in warm springs and delayed flows in cool springs. Furthermore, when springs are aggregated into warm and wet, cool and wet, warm and dry, and cool and dry categories distinct estuarine stream flow and salinity patterns emerge. These four categories also show an oceanic connection: highest coastal sea level heights and lowest sea surface salinities occur during wet (cool and warm) springs and lowest heights and highest salinities occur during cool and dry springs.

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TITLE: Fate of Organic Chemicals in Subsurface Environments

PROJECT NUMBER: WR 71–068

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

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

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

PROGRESS: The movement and fate of the major water soluble compounds of creosote are being studied, both in the laboratory and at the U.S. Geological Survey Hazardous Waste Study Site at Pensacola, Fla. Adsorption characteristics onto aquifer material have been determined for 22 different creosote derived compounds. The kinetics and pathways of transformation under methanogenic conditions have been determined for 12 of creosote derived compounds. Thermodynamic principles have been applied to mechanisms of biodegradation and have revealed that the micro-organisms from the study site have developed the ability to survive in oligitrophic environments by altering their enzymatic capabilities. The organisms have developed the ability to use 99+ percent of the energy available in the organic compounds for maintaining cellular integrity.

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TITLE: Availability of Trace Elements in Sediments to Aquatic Organisms

PROJECT NUMBER: WR 75–125

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

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

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

PROGRESS: Completed experiment on differences in metal bioaccumulation among three species of hydropsychid caddisflies (the most cosmopolitan river biosentinel) in Clark Fork River, Mont. Manuscript in progress on biological processes influencing bioaccumulation in Clark Fork River. Completed experiments and submitted paper on Se bioavailability. Demonstrated differences in availability from different food types and showed that dominance of food pathway in uptake makes systems more vulnerable to Se than predicted from traditional toxicity tests. Demonstrated that differences in digestive processing explain differences in C and Cr assimilation between deposit feeding and filter feeding bivalves (Manuscript submitted). Began experiments comparing Cr assimilation among several food types important in nature (again comparing the two bivalves); intend to model food versus solute pathways and compare to nature as was done with Se. Collected monthly samples as part of characterization of metal contamination in seven populations of *Potamocorbula amurensis* in San Francisco Bay, contributing to San Francisco Bay toxics study. Conducted experiments comparing bioaccumulation in field between Potamocorbula and other bivalves. These experiments will tie with lab studies of metal assimilation and metal bioconcentration. Early results demonstrated element-specific distributions of contaminants in San Francisco Bay, and helped locate populations differing in contaminant exposure for use in physiological effects studies. Determined historic trace element contamination trends from analysis of core materials as part of San Francisco Bay toxics study, and began to try reconstructing benthic community before 1850 from shells in core materials. Helped with the conceptualization and initiation of the U.S. Geological Survey's National Water Quality Assessment Program (NAWQA). Analyzed trace elements in tissues from NAWQA pilot site in Yakima River, Wash. (1989, 1990). Participated in NAWQA Yakima field work. Continued theoretical work on how metals influence biota within the context of other influential processes in nature.

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TITLE: Effects of Toxic Substances on Aquatic Communities

PROJECT NUMBER: WR 75—137

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PROBLEM: Water pollution is principally a biological problem in that its primary effect is on aquatic organisms. Yet, most pollution assessment emphasizes the measurement of chemical and physical variables rather than responses of aquatic organisms to these variables. There are several reasons for this contradictory emphasis on physicochemical 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 physicochemical factors affecting responses and bioaccumulation of these toxic substances. 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: Needs of the ecological survey element of the U.S. Geological Survey's National Water Quality Assessment Program (NAWQA), as defined by program planners, the National Research Council (in its 1990 review), and project staff (in several memoranda) provided the focus for our project activity the past year. Current project research provides a framework for elucidating spatial (biogeographic) patterns in the distribution of benthic communities (algae and benthic invertebrates) of streams and rivers in NAWQA study units. The approach was evaluated in the San Joaquin River (California) and Yakima River (Washington) basins, drainages with two very different hydrologic regimes. Substantial progress also has been made in developing a rapid, practical approach to synoptic measurement and evaluation of physical habitat and hydraulic characteristics in streams and rivers over a range of ecoregions, lithology, valley bottom form, gradient, discharge, substrate, and large woody debris loading. A large component of the variation in aquatic community structure of streams and rivers is associated with differences in physical habitat and discharge. Therefore, knowledge of these habitat characteristics is critical to the interpretation of the biological data.

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TITLE: Biotic Response to Climatic Variability and Human Impacts in arid lands

PROJECT NUMBER: WR 76–145

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

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

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

PROGRESS: Fire and flood regimes integrate weather phenomena over space and time and thus offer a less equivocal measure of climatic variability than point rainfall. Pacific climate, specifically the Southern Oscillation (SO), exerts a strong influence in the southwestern United States, where fires and floods are primary concerns of watershed management. Diagnostic studies of fire and flood climatologies were completed to improve long-term forecasts of large fires and to challenge indiscriminate use of standard methods for estimating flood frequencies. The Project is the principal monitor of some of the oldest vegetation plots in the world, located on the grounds of the University of Arizona's Desert Laboratory. This monitoring has allowed quantification of the rates of invasion of introduced plants over an 80-year period. Climate appears to modulate both the nature and rates of these plant invasions. A climatic scenario involving greater importance of summer versus winter precipitation could lead to the Africanization of the Sonoran Desert, with African grasses replacing native flora. An even longer term perspective on vegetation change comes from packrat middens, the focus of a definitive volume published this year. A related study casts doubt on theory about the genetic consequences of founder (long-distance dispersal) events.

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TITLE: Plankton Dynamics in Tidal Estuaries

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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: Field activities focused on: (1) background hydrographic measurements in San Francisco Bay as part of a multidisciplinary research program (including the Surface Water Toxics Program on San Francisco Bay); (2) an intensive, multidisciplinary and multi-institutional study to measure ecological and biogeochemical responses to the spring phytoplankton bloom in South San Francisco Bay; (3) exploration of biogeochemical indicators (stable isotopes of C, N; lipidbiomarkers) to characterize spatial variations in the sources of organic matter ("food") that support populations of consumer organisms in San Francisco Bay; and (4) daily sampling at the IRI site in Minnesota to characterize fluctuations in lake plankton communities at short time scales. A paper, published in the Journal of Marine Research, presents a decade of field observations plus results of a numerical simulation model to demonstrate how fluctuations in tidal stirring lead to fluctuations in phytoplankton abundance and production in estuaries. Other articles were written and submitted for publication on: (1) seasonal changes in phytoplankton patchiness in temperate zone lakes; (2) use of a recirculating flume to measure phytoplankton consumption by benthic invertebrates in tidal estuaries; and (3) reduced phytoplankton abundance and production in upper San Francisco Bay following the invasion and colonization of the estuary by an exotic clam species, *Potamocorbula amurensis*. Project personnel devoted considerable time and energy in the planning of an international scientific meeting--the 11th Biennial Estuarine Research Federation Meeting--to be held in San Francisco in November 1991.

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TITLE: Microbial Biogeochemistry of Aquatic Environments

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

OBJECTIVE: Conceptual models of biogeochemical transformations will be developed by the combination of lab and field experimental work. Lab work will focus on identification of biochemical pathways, isolation and physiological characterization of relevant microbes. Field work will consist of measuring in situ rates of transformations, based on methods developed in the lab. Physical exchanges between components, such as the flux of biogenic gases to/from the atmosphere from water or soil will be quantified.

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

PROGRESS: (1) In situ rates of selenate reduction were measured in many environments and were found to be rapid. The organisms responsible were isolated and their physiology with respect to competing ions (nitrate) studied. Elemental selenium was found to be incorporated into the tissues of filter-feeding clams; (2) Flux of methane, as well as the methane cycle itself, was investigated and quantified in several locations, including three alkaline-saline lakes, and a new subsiding site in the Sacramento Delta region; (3) The buildup and release of reduced components (ammonia, methane, sulfide) as a consequence of a climatic event (El Niño) influencing the physics of exchange at Mono Lake was studied; (4) Organized and chaired the 10th International Symposium of Environmental Biogeochemistry. Theme: Global Change and the Biogeochemistry of Radiative Trace Gases; (5) Patent awarded on process of selenate reduction. Patent applied for on design for digestion plant.

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TITLE:	Biotic Interface with Fluvial Transport: Processes Associated with Dissolved Solutes in Transport
PROJECT NUMBER:	WR 84—186
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PROBLEM: Biogeochemical processes associated with the microbial community (algae, bacteria, fungi) constitute the interface between solute transport and biotic production in riverine environments. Identifying and estimating 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: Laboratory experiments using communities collected from small to large streams and in situ field experiments are used to estimate biotic transformation of dissolved solutes. Field experiments are conducted at background concentrations and with mixtures of conservative and nonconservative solutes injected into both pristine and man impacted fluvial environments. Cycling of elements which have high assimilative demand and (or) are subsequently passed to higher trophic levels are emphasized (i.e., C, N, P).

PROGRESS: Studies at Little Lost Man Creek, a cobble-bed stream in northern California, reveal a complex connection between channel hydrology and biotic nitrogen cycling. Biotic nitrogen transformations (nitrification-denitrification) occur in a pattern related to dissolved oxygen concentration, which is in turn regulated by advection of channel water to subsurface habitats. As a result denitrification can serve as a sink for nitrate transported across the ground-water stream water interface while ammonium is nitrified during subsurface transport toward the channel. Little Lost Man Creek has been designated a international UNESCO/MAB (Man and the Biosphere) site.
Studies on the Shingobee River, a sandy bed stream in central Minnesota reveal chemical concentration gradients (0—90 cm depth) in sediments. Ferrous iron, conductivity and

ammonium increase with depth whereas nitrate and dissolved oxygen decrease. Nitrification potential in slurries from sediment cores indicate significant activity except when inhibited with nitrapyrin. Denitrification potential was low but measurable. Comparison of summer and winter nutrient concentrations indicates extensive potential for uptake by channel macrophytes and riparian vegetation.

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TITLE: Solute Transport Involving Biological Processes in Surface Waters

PROJECT NUMBER: WR 86–190

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PROBLEM: Availability of toxic substances and nutrients to biota is dependent on their chemical form or speciation. Toxicological models, for example, have emphasized the effect of solute speciation on biological processes. Conversely, it has been demonstrated that partitioning of contaminants and nutrients can be affected by biological processes. Chemical processes that control chemical speciation in natural waters are solute complexation, precipitation/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: Reports have been published or are in review for journal publication presenting resulting from metal and macronutrient distribution studies. A report on the development and application of hollow-fiber, tangential flow technology for collection of bacteria and suspended particulate matter was published. The work has generated international interest and application of this technology. Another report presenting an initial trace metal data set for streams flowing into Lake Tahoe, Nevada/California, has been published and was well reviewed. The distribution and concentration of trace metals, macronutrients, dissolved organic carbon, ATP and phytoplankton size and biomass distributions were compared between a nearshore (180 meter depth) and midlake (450 m depth) station at 5 depths at Lake Tahoe, Calif./Nev. Results of field data combined with bioassay experiments designed to identify possible limiting or toxic trace solute effects suggested that while phytoplankton may be phosphate limited, periodic iron limitation is also likely. The results demonstrate that in an oligotrophic system such as Lake Tahoe, solute concentrations are at a fragile balance. Small perturbations in water chemistry (both observed natural and anthropogenic) have pronounced effects on biological parameters. Collaborative work with Professors Richard Petersen and John Rueter of Portland State University will determine phytoplankton abundance (including picoplankton), distribution and productivity in both Lake Tahoe (presumably P-limited) and Crater Lake (N-limited). New techniques have established the existence of picoplankton, which account for a large part of photoautotrophic carbon reduction, particularly in oligotrophic waters and at low levels of irradiance. Our present studies of nutrient interactions in lakes has been extended by contrasting iron limitation, on an cellular level, of phytoplankton from Lake Tahoe, Calif./Nev., and Crater Lake, Oreg., (contrasting macronutrient interactions). Collaborative work with Thomas Tisue, Clemson University, on sediment transport within Lake Tahoe (Cd-113 work) and on the importance of sediment resuspension as an important nutrient source for the Lake Tahoe is now being written. A polarographic method, adapted from marine studies, is developed and in use for determination of dissolved sulfides in oxic waters (detection limits of approximately 1 nM). Measurements made during the winter of 1990 and spring of 1991 in the northern and southern components of San Francisco Bay indicate that sulfides exists at concentrations that may significantly affect metal speciation (and hence, bioavailability) in the oxic water column. However, dissolved sulfides concentrations were typically not high enough to disregard competitive reactions between metals and dissolved organic matter.

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ECOLOGY

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

PROJECT NUMBER: WR 86-191

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

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

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

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

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TITLE: Environmental Influences on Estuarine Benthic Community Dynamics

PROJECT NUMBER: WR 86—192

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

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

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

PROGRESS: During FY91 we continued studies of *Potamocorbula amurensis*, the clam recently introduced into San Francisco Bay, to document its spread and impact. A paper, in preparation, shows that it has not been equally successful in its spread throughout the bay. Some communities of the bay have been less prone to invasion possibly due to the presence of tube dwelling organisms which may be able to exclude juveniles from settling in these areas. We do have evidence that *Potamocorbula* can successfully compete and coexist with other major bivalve filter feeders in the bay but there may be intraspecific competition as adults may inhibit juveniles from settling in the more densely packed *Potamocorbula* populations. This paper describes the invasion pattern of this species in several different communities of the bay and how this pattern compares with invasions by introduced species in other systems. Studies of the filtration rate of this clam have resulted in a new protocol for measuring filtration rate of infaunal invertebrates in laboratory flumes. A paper describing this protocol has been submitted to the journal Marine Biology. Collaboration with researchers at Stanford University, who are looking at the hydrodynamics of filter feeding using models of the bivalves which we are using, has established the importance of certain hydrodynamic properties (bottom roughness and siphon height and orientation) in our flume studies. To quantify the ecological responses to organic contaminants in the benthic community, we are characterizing the long-term patterns of benthic community composition at seven fixed sites in northern San Francisco Bay to define the relationships between community structure and natural environmental perturbations, for example, responses to short- and long-term variations in river flow (changes in climate and subsequent alteration of salinity regime). As part of the Toxic Substances Hydrology Program in the bay, we are studying the reproductive cycle of the dominant benthic organism (*Potamocorbula*) throughout the salinity range of the bay to determine the effect that contaminants might be having on the reproductive condition. The benthic communities at eight south bay locations are being monitored to determine how the spring phytoplankton bloom effects the growth cycle of the individual species. The primary factor in the development of this bloom is the stratification of the water column which separates the growing phytoplankton cells from the bottom organisms. Under normal mixed conditions in the water column, these animals consume phytoplankton as fast as they grow. It is of particular interest that the responses of organisms at the shallower stations may differ in timing and magnitude from those found in the deeper water. This difference maybe related to the physical transport of the phytoplankton to the shallow bottom organisms both during and after the bloom, whereas the deeper communities may have access to the accumulated phytoplankton only after the breakdown of the water column stratification.

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GEOMORPHOLOGY AND SEDIMENT

TITLE: Movement and Storage of Sediment in River Systems

PROJECT NUMBER: CR 75–102

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

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

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

PROGRESS: One sampling cruise was completed on the Mississippi River between Minneapolis, Minn., and New Orleans, La. A resurvey of cross sections in Powder River, Mont., showed small to moderate amount of channel change since last year.

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GEOMORPHOLOGY/SEDIMENT TRANSPORT

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TITLE:	Effects of Water and Sediment Discharges on Channel Morphology
PROJECT NUMBER:	CR 65–105
PROJECT CHIEF:	Williams, Garnett P.
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PROBLEM: Channels on alluvial streams change with time. Bed elevations and channel widths may change, meander bends shift both laterally and downstreamward, the sizes of the bed particles may change, instream bars grow and migrate, and the amount and type of vegetation along the river may increase or decrease. Sometimes the change is minor and insignificant, even over decades, but in other cases catastrophic modifications occur in minutes. The transformations can be natural or man-induced, and they can have significant effects on man and the environment.

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

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

PROGRESS: Proportions of bedload to total sediment load in rivers vary widely from one time to another at a cross section, from one cross section to another on the same river, and from one river to another, even within the same geographic region. The bedload proportion at most sites showed no significant relation to: (a) suspended sediment concentration, (b) flow depth, (c) channel width, or (d) channel shape (width/depth ratio).

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TITLE: Hydraulics and Mechanics of Bedload-Transport Processes

PROJECT NUMBER: CR 74–187

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

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

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

PROGRESS: (1) Field work at the bedload trap and for the fluorescent-tracer study is complete. Bedload-transport rates measured synoptically, vary along a river reach; bedload tonnage, measured seasonally, is about constant throughout the reach. Mean bedload-transport rates relate to streampower (about the 1.6 power of streampower in excess of streampower at initiation of motion), mean bedload-particle speeds are slow (about 0.1 percent of water speed), and lengths of particle movement may be seasonally limited. (2) Radio transmitters were implanted in cobble-size rocks and movements tracked as part of studies on Toklat River, Lignite Creek, and Phelan Creek, Alaska. Bedload-transport rates relate about to the 1.6 power of discharge in excess of discharge at initiation of motion and particle size (mean, modal, and maximum) increased as transport rate increased. Motion sensors allow distinction between periods of motion and periods of inactivity. Generally, brief periods of motion are followed by longer times of rest. Large moving particles (about fist size) travelled about the same distance as smaller particles (about golf-ball size). Particle speeds and distances travelled are in general agreement with observations from East Fork River, Wyoming (3) Long-term data collection continued for the ninth year at Little Granite Creek, Wyoming (in cooperation with the Idaho District, U.S. Geological Survey). Although measured total-sediment loads are among the longest data sets available at a continuous-record gage, the period of record is still short to forecast time trends. Generally, during the period of observation, water runoff has decreased and sediment yields have lessened more dramatically. These facts may be related to short-term weather variability rather than to long-term climate change. (4) Comparisons of equipment and procedures were continued in collaboration with personnel in other countries and from other U.S. Geological Survey offices. (5) In collaboration with other USGS scientists and academia personnel, environmental assessments were conducted on several streams in Yellowstone and Denali National Parks, Wyoming and Alaska. A field procedure to evaluate habitat quality was developed combining geomorphic aspects (river hydraulics, sediment characteristics, topography), water chemistry (pH, conductance, trace elements, organic carbon), and biological factors (benthic drift, invertebrates, fish). (6) Studies of phytoplankton taste and odor problems were established on Fremont Lake; interpretations are in progress.

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GEOMORPHOLOGY/SEDIMENT TRANSPORT

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

PROJECT NUMBER: CR 81–266

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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 sub-bottom profiling). Analyze sediment samples for indicators of sources (particle size, mineralogy, nutrient and trace-metal concentrations) and accumulation rates (lead-210, 14C 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.

GEOMORPHOLOGY/SEDIMENT TRANSPORT

PROGRESS: The 1990 water-year was again a period of extensive high water and overbank flooding in the Mississippi River study area. Except along natural levees and steep banks adjacent to the modern channel, deposition of fine-grained sediments controlled by elevation and topography was the dominant sedimentation phenomenon. Extensive erosion of unprotected channel margin banks resulted in up to 3 meters of bank retreat and loss of highly productive crop land. Natural levees in many areas were extensively modified by overbank flows; deposition of coarse sediments prevailed in some areas, but erosion occurred in other areas. Extreme local variability in natural levee areas often appeared to be related to transport and accumulation of logs and other debris. Along protected banks, local pockets of mostly coarse sediment developed after some high stages, but were sometimes removed and didn't develop after the next high stage. In general, it appears that sedimentation along steep channel margin banks may be controlled by the rapidity of rising and falling stage. Efforts to estimate long-term deposition rates using dendrogeomorphic techniques meet with mixed success. In many locations, high and variable deposition rates resulted in development of many zones of adventitious roots that made digging and recognition of an original root zone difficult. A report on Potomac River and estuary sedimentation was completed and revised after colleague review.

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TITLE:	River Mechanics
PROJECT NUMBER:	CR 82—273
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PROBLEM: The geometry and pattern of river channels adjust to significant changes in the water discharge, size, and quantity of sediment supplied to the channel. When the quantity of water and sediment over a period of years remains relatively constant, the channel geometry and pattern vary about a mean or quasi-equilibrium condition. Major watershed alterations that change the supply of water, sediment, and size of sediment reaching the channel necessitate an adjustment of the channel geometry and pattern. That is, the channel is transformed from one quasi-equilibrium state to another. Between the two quasi-equilibrium states, there is a period of instability. Existing techniques for examining and predicting river channel adjustment have been developed primarily from investigation of quasi-equilibrium rivers. As a result, it is frequently possible to predict with a modest range of uncertainty the future quasi-equilibrium hydraulic characteristics of a river following a change in its watershed. The dynamics and rate of river channel adjustment during the period of instability however, have rarely been studied, and are rather poorly understood. The length of time required for the complete adjustment is commonly a few decades to a century or more. In many instances, such as surface mines, reservoirs, and urbanization, the adjustment period may, in fact, be longer than the duration of the watershed change. In watersheds where various land-use changes occur every several years, river channels may be continually adjusting to different contributions of water and sediment, and thus, never reach a quasi-equilibrium condition. In these rivers, instability is the only significant condition. Consequently, an understanding of the dynamics and rate of river channel adjustment from one quasi-equilibrium state to another is very important to managing fluvial resources. A wide range of social and economic costs may result from significant river channel changes. One of the most frequent and important adverse impacts 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. In order to evaluate the biological impacts of watershed alternation, hydrologists are frequently asked 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 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 appear to be (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: The ideal approach for this investigation would be to observe the transition of a river channel from one quasi-equilibrium state through a period of instability to another quasi-equilibrium state as a result of a known change in the supply of water and sediment. However, this is obviously impractical since adjustment of a river channel may extend from a few decades to a century. Instead, two basic types of field studies will be combined. First, the movement of bed material through a reach of channel will be studied in detail. These investigations will consider the transport of bed material, distance transported, and location (bed, banks, or bar) of deposition for each size fraction. Using measured bedload and suspended transport rates, detailed measurements of flow structure, and mapping of channel features, the movement of bed material through the study reaches will be described. To the extent possible, these observations will be generalized to formulate physically-based models of sediment movement by size fraction. The second part of this investigation will involve reconstructing the sequence and rate of adjustment for historical examples of river channel change. Because of the lack of detailed hydraulic measurements, this portion of the investigation may at times be somewhat descriptive and qualitative. These observations, however, will be vitally important, as they will provide the temporal context in which to view the hydraulic characteristic at a particular point in time.

PROGRESS: During the 1990 fiscal year, significant progress has been made in several areas: flow over bedforms, roughness of poorly sorted beds, incipient motion and marginal sediment transport rates in natural streams, and lateral separation eddies. Ongoing research on the flow and turbulence structure over two-dimensional bedforms led to a recognized need for a larger facility in which to make laboratory measurements. A cooperative effort with University of California at Santa Barbara (UCSB) was initiated and a proposal to the National Science Foundation to fund this laboratory work was prepared. This proposal was funded for a 3-year period beginning in October of 1989. Since then, a computer operated laser-Doppler velocimeter has been assembled at UCSB and a 20 meter flume has been prepared for these experiments, which began in August of 1990. Preliminary measurements have substantially improved our understanding of the turbulence structure of flows over bedforms. The work on roughness of poorly sorted beds is directed toward developing a thorough understanding of grain roughness on naturally-emplaced sediment beds. The first stage of this work consisted of a series of flume experiments wherein measurements of velocity and Reynolds stress over beds composed of well- and poorly-sorted material were made in order to assess bed roughness. Sections of the flume beds were preserved and current work is focussed on the development of stereo-photographic techniques for the determination of bed roughness. In addition, theoretical calculations of roughness and velocity profiles over rough beds have been performed. This work has produced computational models capable of accurate predictions of stage-discharge relations in steep, coarse-bedded channels. This work was also extended to the problem of making accurate predictions of the bed-material transport rate when only a small fraction of the bed particles are entrained at a given time. Bed material transport rates were sampled at five sites in the Front Range of Colorado during the spring of 1989. Using this information a significant improvement in the computation of coarse particle transport has been made. The work on lateral separation eddies consists of a combination of field, laboratory, and theoretical work aimed at understanding the mechanics of flow and sediment transport mechanics in separation eddies. One flume experiment has been completed, and several sites have been studied and analyzed for suitability as sites for a comprehensive field study. A current metering system for this work is being developed in cooperation with the University of Washington. In addition, a numerical model for flow in lateral separation eddies has been constructed and is currently being debugged and prepared for testing in laboratory and natural eddies.

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TITLE: Sediment-Transported Pollutants in the Mississippi River

PROJECT NUMBER: CR 87—309

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

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

APPROACH: Make two to three boat trips per year, beginning above St. Louis, Mo., and ending at New Orleans, La., 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 constituents, both natural and manmade.

PROGRESS: A substantial increase in project funding was received, along with a Congressional mandate to extend the project scope to include the upper Mississippi River. Backlogs of analytical work on samples collected during the first seven cruises (1987—1990) were cleared through the laboratories of the participating chemists. Numerous visits were made by project members to agencies to confer with U.S. Fish and Wildlife Service, Corps of Engineers, and agencies of the upper-river states, especially Minnesota, Wis., and Iowa. One full-scale chemical sampling trip on the Mississippi River between Minneapolis, Minn., and New Orleans, La., was completed between June 23 and August 7, 1991.

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TITLE: Sediment Impacts from Disturbed and Undisturbed Lands

PROJECT NUMBER: CR 79–311

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

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

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

PROGRESS: Research was completed on the use of beryllium-ten as a natural tracer of sediment movement on the Southern High Plains of Texas and New Mexico. This research demonstrates the use of the isotope to trace eolian transport of sediment and the recharge of ground water through the unsaturated zone. Similar techniques were begun to estimate transmission losses and recharge from ephemeral-stream channels using beryllium-ten at the Nevada Test Site and in the United Arab Emirates.

During fall 1990 and spring 1991, field work was initiated in several localities in the upper South Platte River basin, including Plum Creek, Coal Creek, Turkey Creek and Tucker Gulch. Research on the fluvial geomorphic history of Arthurs Rock Gulch was continued. The emphasis of field investigations was to document the spatial distribution of Holocene fluvial deposits, and to begin work on the geochronology and sedimentology of these deposits. Multiple episodes of overbank-and flash-flooding were recognized in the areas investigated and numerous samples were collected for radiocarbon dating. Radiocarbon ages will be used to determine the temporal framework of alluvial activity in the study area, and a means for correlation of alluvial stratigraphic and proxy paleoclimate records.

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TITLE:	Sediment-Water Chemistry in Large River Systems: Biogeochemical, Geomorphic, and Human Controls
PROJECT NUMBER:	CR 88-313
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PROBLEM: Rivers are a major pathway to the ocean for erosion products and human wastes. The mechanisms that control the composition of river-borne materials are only imperfectly understood because erosion and the subsequent transport of material by rivers are mediated by a wide variety of closely linked chemical, biological, and physical processes. Moreover, in developed river systems such as those in the United States, these processes are subject to pervasive human-related perturbations. There is a need to develop, through field and theoretical studies, a comprehensive and integrated description of these processes for large river systems in a form that is useful to researchers in many disciplines.

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

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

PROGRESS: In FY-1991, project efforts focused on initiating research, related to the Global Change Program, on the biogeochemistry of humid tropical watersheds. Research is concentrated on investigations of nutrient cycles, gas exchange, and weathering and erosion processes in small watersheds in northeastern Puerto Rico, at the Luquillo Experimental Forest (LEF), and in central Panama, at the Barro Colorado Nature Monument (BCNM). The LEF is the site of a recently initiated project funded under the Water, Energy, and Biogeochemical Budgets (WEBB) Program of the U.S. Geological Survey, Water Resources Division (WRD) and run through the Caribbean District Office of WRD. The BCNM is under the stewardship of the Smithsonian Tropical Research Institute (STRI) which presently shares funding for the work. The experimental is designed to compare natural and developed environments. Sampling is organized using a quasi-nested-basin approach. Microwatersheds have been selected on contrasting lithologies. The microwatersheds are used to identify and characterize processes in detail. Larger watersheds are used for the hydrologic and chemical budgets, because the spatial distribution of agricultural development and of many important hillslope processes, such as landslides, is sufficiently patchy and uneven that it is impossible to select representative micro-watersheds. The larger watersheds are contrasted with geologically matched nearby watersheds that have been agriculturally developed. The primary objective of the studies of weathering and erosion is to use long-term chemical sampling and physical monitoring to characterize the processes that control the distribution and transport of major, important-minor, and nutrient elements through soils, downslope, and out of the watershed. Phenomena of interest to global-change research include the fixation, storage, and export of carbon and nutrients as related to biogeochemical and geomorphic processes within the watersheds. Research efforts are apportioned between the study of soil-sediment-water interactions and the study of atmospheric trace gas-soil interactions. During FY-1991, there were six field trips to Puerto Rico. Sample analysis and data reduction continues for long-term studies of the Mississippi, Orinoco, and Amazon River systems.

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TITLE: Response of Fluvial Systems to Climatic Variability

PROJECT NUMBER: WR 89-200

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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: A conceptual framework for addressing the spatial and temporal effects of climatic variability on fluvial systems has been developed. Climatic patterns that affect winter flooding in the southwest have been identified, and work is proceeding on identification of the frequency with which this climatic patterns have occurred. Development of a new absolute dating technique involving cesium-137 is proceeding with promising results. This method, when proven, will be used in conjunction with dendrochronology to estimate sediment storage in alluvial channels during the last 50 years. Hydroclimatic analysis of flood frequency is proceeding with efforts concentrated on statistical methods of mixed population analysis. Analysis of frequency of tropical cyclone floods in the southwestern United States is proceeding, with identification of periods of reduced rainfall from this storm type occurring in the Four Corners region of the southwest after 1942. Two publications documenting this work are in press and two are in preparation.

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Page 87 follows

GROUND-WATER CHEMISTRY

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

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

APPROACH: Obtain ground-water samples of interest from the Idaho National Engineering Laboratory (INEL) and possibly other sites. (Other sites have not been selected, but one possible site under consideration is the Underground Research Laboratory at the Whiteshell Nuclear Research Establishment, Pinawa, Manitob). Add known quantities of plutonium, pre-adjusted to the reduced [Pu(III) and (IV)] or oxidized [PuV) and (VI)] forms to measured volumes of each of these waters, place in tightly sealed Teflon vessels, and allow to stand in darkness for periods of 3, 7, 17 and 30 days. At the conclusion of the specified time period, mix well, sample, filter through a 0.1-micrometer filter and sample again. The plutonium in the filtrate is defined as being soluble. Determine the oxidation-state distribution of the soluble plutonium by carrier precipitation and solvent extraction techniques. Repeat the solubility determinations using americium(III). Run five replicates at each set of parameters. Attempt to correlate plutonium solubility and oxidation-state distribution and americium solubility to the chemical composition and redox properties of the ground water.

PROGRESS: Studies have concentrated on ground waters from the Radioactive Waste Management Complex (RWMC) at the Idaho National Engineering Laboratory (INEL). Speciation/solubility studies on plutonium and americium were conducted on seven ground waters from RWMC, specifically the production well and wells 87, 88, 89, 90, 117, and 120. In the high-oxidation-state runs, plutonium was soluble in all the waters, whereas varying results were obtained in the low-oxidation-state runs. Plutonium was most soluble in production well water (72 percent after 30 days) and was present primarily in the high oxidation states; it was least soluble (18 percent) in well 88 water. Plutonium solubilities in the other waters ranged from 34 to 60 percent, and in 5 of the waters studied Pu(IV) was the predominant oxidation state—an unexpected finding. Because the chemical compositions of the waters were similar and unremarkable, it was concluded that the variations in plutonium solubility were caused by differences in the redox properties of the waters. Americium solubilities were relatively low (less than 40 percent) in all waters, and lowest of all in well 88 (9 percent). We concluded that although solubilities in some cases are limited, they are always high enough to cause a significant migration potential.

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TITLE: Geochemistry of Clay-Water Reactions

PROJECT NUMBER: CR 82–276

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PROBLEM: Clay minerals can influence the chemistry of ground water and other aqueous solutions through precipitation, dissolution, and ion-exchange reactions. An understanding of these reactions is crucial for predicting the behavior of toxic wastes in disposal areas. How do the various clays react with waters of varying composition at different temperatures and pressures? After the fundamentals of these processes are understood, how can they be applied to prediction, 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: We continue to work on slow-release, nonpolluting fertilizers. A slow-release N-fertilizer is in the final stages of the patent application process. We manufactured one ton of this fertilizer for experimentation during the 1991 growing season at the MSEA sites in Missouri, Iowa, and Nebraska and for green house experiments at Colorado State University. We also discovered and plan to patent new type of slow-release P-fertilizer that uses low-grade P rock and can be used in conjunction with the N-fertilizer.

Our project has discovered that many minerals in sedimentary and metamorphic environments react by Ostwald ripening (cover article in Science in April, 1990), and that, as a consequence of this ripening, they contain a detailed record of their recrystallization history. Currently, we are extending our knowledge of the ripening process by: (1) trying to derive a common rate law for this recrystallization; (2) running hydrothermal experiments (with Whitney, Geologic Division) to measure rate constants and activation energies for illite recrystallization (year-long experiments due out in August, 1991); (3) working on methods for measuring particle size distributions for clays (a necessary step for studying minerals that have ripened), including use of the Atomic Force Microscope (with Alex Blum) and Field Flow Fractionation (with Howard Taylor); and (4) separating natural clays into various size fractions, and then studying their structure, chemistry and isotopes (with Polish geologist Jan Srodon and a French postdoc who works with our project, Bruno Lanson).

We have continued with clay mineral sample collection, preparation and characterization, for calorimetry and solubility experiments pending occupancy of adequate laboratory facilities at Boulder. We have developed a new free energy of formation data set for kaolinite and dickite, and are currently refining values in the data set to account for the diluting effects of impurities. An investigative comparison of surface area measuring techniques, and their resultant values for external, internal and total surface areas of clays has begun; this study can relate surface area measurements to reactive (effective) surface area and to mineral reaction kinetics.

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TITLE: Environmental Dynamics of Persistent Organic Compounds

PROJECT NUMBER: CR 83–283

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PROBLEM: Many persistent organic compounds are hazardous to human and ecological health. The transport characteristics of the compounds across environmental phases are strongly influenced by adsorption 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: The surface area of soil organic matter (SOM) was measured by the standard BET (nitrogen adsorption) method. The observed small BET surface (about 0.7 m sq/g) for SOM suggests that organic compound uptake by surface adsorption on SOM is practically insignificant in comparison with uptake by partition, which is consistent with our earlier postulate and should further clarify the confusion that persists until today. The enormously large surface area for SOM reported by others based on the retention of ethylene glycol (EG) is considered to be an artifact of the calculation method, which erroneously assumed surface adsorption of EG rather than bulk solubility in SOM. In another study, we investigated the effect of residual oil in commercial linear alkylbenzene sulfonate surfactants (LAS) on the organic solute water solubility. The residual oil content in LAS was found to be about 1.7 percent by weight of the active ingredient. The order-of-magnitude water solubility enhancement of DDT and PCB by LAS below its critical micelle concentration (CMC) is ascribed to the formation of oil-surfactant emulsions which function as a bulk organic phase. The emulsion mass was about 9—10 percent by weight of the LAS active ingredient. The data suggest that discharge of wastewater containing a significant level of oils and surface-active agents would lead to potential mobilization of organic pollutants in aquatic environments.

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TITLE: Reaction-Transport Modeling in Ground-Water systems

PROJECT NUMBER: CR 89–318

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

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

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

PROGRESS: Work on the Central Oklahoma National Water Quality Assessment (NAWQA) has resulted in the preparation of a Water-Supply Paper, now in draft form. The paper describes one of the first times a ground-water flow model has been calibrated using carbon-14 dates of ground-water age. Mass-balance calculations presented in the paper show the dominant reactions in the ground-water system are carbonate dissolution and cation exchange. The mass-balance calculations were performed with a new version of the program BALANCE, which accounts for uncertainty in the analytical data. Extremely oxidizing conditions occur in the aquifer, which provide an environment conducive to large concentrations of arsenic, chromium, selenium, and uranium. Preliminary plans have been made to hold a workshop for researchers interested in coupling geochemical reaction models with solute transport models.

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TITLE: Mineral-Water Interaction in Saline Environments

PROJECT NUMBER: NR 69—020

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

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

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

PROGRESS: The normative and isotopic appraisal of central Murray Basin, Australia, ground waters is in further revision, with an attempt at detailed comparison with solute modification processes in the Yilgarn block of western Australia. The sorting out of mixing in ground waters variably concentrated by evaporation before recharge, and separation of weathering versus aerosol or diagenetic contributions has become quite complex. At the same time, major effort was continued on normative and bi-variant analysis of brine data from the Salada Formation and underlying strata at the Waste Isolation Pilot Plant (WIPP) site, southeast New Mexico, in collaboration with Scott Anderholm of the New Mexico district. These results seem to clearly identify formationally distinct brines, and naturally-occurring from anthropogenically-affected fluids in the repository horizon. In addition, a brief summary of the last 5 years of Water Resource Division (WRD) research at WIPP (including the district density driver ground water flow modeling) was completed.

In conjunction with U.S. Geological Survey/Spain investigations of geochemical reactions and transport in regional aquifer systems, additional work has been accomplished on hydrochemical mass balance modeling for the clastic aquifer of the Madrid Masin, with its complex alluvial and lacustrine sediments, calcretes, and clay mineral assemblages, and will be compared to U.S. Great Basin examples. A survey of isotopic and minor element distributions in the carbonates was completed with Spanish colleagues. The compositional variations introduced by the focus on silicate reactions are being pursued with new spreadsheet and advanced mass transfer, solid solution, and isotopic balance programs. With Professor C.J. Bowser, University of Wisconsin, a general scheme taking advantage of the readily available X-cel personal computer software and graphics is being tested for a variety of cyrstalline rock-dominated drainage basins.

Transmission and analytical electron microscope studies with J. Banfield and Professor D. Veblen at Johns Hopkins University has further defined the weathering and diagenetic reactions of volcanics and associated saline lacustrine sediments at Abert Lake, southcentral Oregon, confirming and significantly extending our earlier findings on controls of major cations in water by smectite clays. A major two-part manuscript was approved for publication.

The ultrafine particulate mineralogy in west Texas saline lake cores has documented cycles in clay-mineral species dominance that can be related to variation in lake level through previously project-developed theory detailing the hydrologic controls on magnesium clay formation. The clay mineralogy of core samples from Lake Baikal was found to be essentially detrital, but variably obscured by iron oxide accumulations.

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GROUND-WATER CHEMISTRY

TITLE: Spatial Distribution of Chemical Constituents in Ground Water

PROJECT NUMBER: NR 57–034

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PROBLEM: Reactions and processes that control the chemical character of ground water need to be identified to predict physical and chemical changes that occur in natural and stressed environments. This project focuses on effects of these reactions in (1) regional limestone aquifers, 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: For the past year, this project has been devoted largely to editing books, writing review articles, organizing international symposia, and giving lectures. The fieldwork was with Janet Herman, where we are looking at the mineralogic changes as a function of chemistry of water in a limestone sequence in west-central Florida. This work is still in the stage of field sampling and laboratory analysis.

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TITLE: Interface of Paleoclimatology and Aquifer Geochemistry

PROJECT NUMBER: NR 74—041

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PROBLEM: Reconstructions of continental paleoclimates of the Pleistocene Epoch have relied almost exclusively on lacustrine, packrat-midden, and speleothem 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 paleoceanographic studies; (3) differentiate between, and determine relative magnitude of, summer and winter recharge to major uplands; 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) Four papers summarizing our latest paleoclimatologic findings from Devil's Hole, Nev., core DH—11 were presented at the 1990 annual meeting of the Geological Society of America by Messrs. Winograd, Coplen, Landwehr, and Ludwig; these presentations generated lively discussions with adherents of the Milankovitch theory. (2) The four oral reports are being prepared for submittal to and publication in Science. (3) Two papers were published on technical and philosophical facets of the Yucca Mountain endeavor.

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TITLE: Kinetics and Thermodynamics of Chemical Evolution in Ground-Water Systems

PROJECT NUMBER: NR 76—056

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

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

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

PROGRESS: Research continued on assessment of the capabilities of CFCs as a tracer and age-dating tool for modern groundwater. More than 130 wells were sampled for CFCs, D, ^{18}O and tritium in November (1990) and April (1991) in the Delmarva (Delaware-Maryland-Virginia) Peninsula National Water Quality Assessment (NAWQA) study site. Recharge temperatures determined from dissolved nitrogen and argon concentrations range from 4 to 12 °C from the northern to southern tip of Delmarva and are similar to the latitudinal variation of late-winter to early-spring mean air temperatures in Delmarva. Excess air entrained in the recharge process is 0 to 3 cm^3 per liter. Preliminary tritium data adjusted for radioactive decay using the modeled CFC ages correspond closely to the expected tritium input function between 1960 and 1990. The CFC ages are also consistent with known hydrology, and the known dates of introduction of nitrates and pesticides in Delmarva. Work continued in the central Oklahoma NAWQA study site where approximately 60 surface waters were analyzed for CFCs. CFC concentrations several orders of magnitude greater than air-water equilibrium were found associated with effluent from sewage treatment plants. It is likely that treated sewage effluent is the source of the previously recognized anomolies of CFCs in shallow ground water of the Alluvium and Terrace deposits along the rivers. Other extensive sampling for CFCs was conducted at (1) Idaho National Engineering Laboratory (INEL), (2) Culpepper Basin of Northern Virginia, (3) poorly confined portions of the upper Floridan aquifer in north-central Florida, and (4) the Floridan aquifer at Valdosta Georgia which receives point source recharge through sinkholes in the Withlacoochee River. The INEL waters appear to be mixes of pre-1940 water and CFC-contaminated water. The recharge temperatures determined by dissolved gas analyses were equal to the mean annual temperature, as expected for recharge through the deep unsaturated zone at INEL. CFCs were found to depths of 1,000 feet in fracturated rock of the Culpepper Basin. Other studies focused on interpretation of (1) a reverse paleoclimatic trend in stable isotopes found in the Floridan aquifer of the Coastal Plain of Georgia, (2) further development of the NETPATH geochemical modeling code, and (3) study of the dissolution of strontianite-aragonite solid solutions in nonstoichiomentic aqueous solutions. The Georgia Floridan aquifer becomes progressively enriched in ^{18}O and D down the hydraulic gradient, to nearly 2 permil in ^{18}O. Radiocarbon ages are approximately 20,000 years B.P. The enrichment records the isotopic shift of the Gulf of Mexico into the last glacial maximum and may be characteristic of other low-latitude coastal aquifers. The code NETPATH was extended to model the total carbon system (inorganic + organic carbon). The program is used to interactivley construct net geochemical reaction models along flow paths and has extensive radiocarbon age-dating capabilities. Documentation for NETPATH was completed. Work continues on the theoretical and experimental investigations of solid-solution aqueous-solution interactions. A manuscript was completed describing extensive kinetic and thermodynamic experiments on the dissolution of solid-solution minerals in nonstoichiomentric aqueous solutions. Kinetic experiments show that strontianite-aragonite solid solutions dissolve more slowly in nonstoichiometric solutions than in stoichiometric solutions. Experimental attainment of stoichiometric saturation is enhanced by dissolution of solid solution minerals in solutions containing an excess of the more soluble component of the solid. X-ray photoelectron spectroscopy measurements confirm the formation of solid solutions on the surfaces of aragonite and strontianite after only 2 minutes of contact with strontium bicarbonate and calcium bicarbonate solutions, respectively. A review was made of the distribution coefficient literature on the $KCl-KBr-H_2O$ and $NaCl-NaBr-H_2O$ systems. Good agreement was documented between the excess-free-energy-of-mixing parameters determined for K(Cl,Br) solid-solutions by Glynn and others (1990) and calorimetric and solubility-derived results reported by other authors. Laboratory work determining distribution coefficients for trace Br in NaCl and KCl crystals is also in progress. A preliminary solid-solution version of the computer code PHREEQE has been written and work continues on an implementation into the transport code PHREEQM. A comparative study of various computer codes simulating contaminant transport with chemical reactions is in progress. A simulation of the Pinal Creek, Ariz., toxic-waste site, involving several precipitation/dissolution and redox reactions, was completed showing excellent agreement between the PHREEQM and MST1D computer codes. The DYNAMIX code is also being tested on this same problem. Several new simulation problems have been designed to compare ion exchange algorithms and to establish conditions for which sequential iteration is needed between solution of chemical equilibrium equations and transport equations. Work on the geochemical characterization of the Pinal Creek toxic waste site is continuing. It is suggested that the increase in the Sr concentrations along the flow path of the contaminated ground water is due to Sr contributions from dissolving silicate minerals or exchange reactions rather than from the dissolution of carbonate minerals. The amount of Sr and other impurities incorporated in gypsum precipitated along the flow path is not sufficient to significantly alter the thermodynamic stability of the gypsum. Instead, the gypsum supersaturation observed in Pinal Creek ground waters is thought due to a balance between gypsum precipitation kinetics and the rate of Ca input to the ground water by dissolving minerals.

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TITLE: Physical Chemistry of Stable Isotope Fractionation in Hydrologic Processes

PROJECT NUMBER: NR 75—064

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PROBLEM: The stable isotopes of hydrogen, carbon, nitrogen, oxygen, silicon, and sulfur show variations in their isotope abundances and may be useful in studying evaporation, ground-water mixing, lake or reservoir circulation and stratification, water-acquifer interaction, 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 and dedemonstrate applications in suitable field locations such as intermontane ground-water reservoirs, closed-lake basins, surface-reservoirs, lakes, or estuarine systems to aid in more complete use of light stable-isotope phenomena in hydrologic and paleoclimatic studies.

APPROACH: Analyze water, gas, 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: Carbon and oxygen stable isotopic analyses of calcite vein core DH—11 from Devil's Hole, Nev., show four prominent minima in ^{13}C centered around glacial terminations II through V. These minima may indicate periods of increased effective moisture prior to the beginning of deglaciation with concomitant lowering in elevation of tree lines and expansion of vegetation near Devil's Hole. Three papers were given on Devil's Hole at the Geological Society of America Meeting in Dallas, Texas, in fall 1990 by Reston, Virginia, researchers.

J.K. Böhlke is making excellent progress on nitrogen isotope sample preparation and analysis since his arrival on this project in January. He has found that nitrate-rich caliche samples from the Amargosa, Calif., desert are enriched in ^{15}N relative to those from the Atacama, Chile, desert. These differences may be indirectly related to distance from marine sources or degree of desert aridity. Ground water and the stream water it enters at the Fairmount (Delaware) watershed are distinguishable in ^{15}N content and indicate that future nitrogen isotope studies can provide information on the fate of nitrogen in this coastal plain environment system.

An outgrowth of work on separation of carbon dioxide and nitrogen oxides by K. Revesz lead to identification of Viton and FETFE as materials that fractionate oxygen isotopes of carbon dioxide. Therefore, if stopcocks are used in construction of sample containers for carbon dioxide, the use of all-glass stopcocks with Apiezon N grease will eliminate the fractionation of oxygen isotopes.

Working with M.J. Baedecker, K. Revesz is making good progress on investigating the carbon and hydrogen isotopic composition of methane in the saturated zone, the unsaturated zone, and the atmosphere at the toxic waste site at Bimidji, Minnesota.

We published our gaseous hydrogen-water equilibration technique for hydrogen isotopic ratio analysis of water samples. This technique essentially doubles the throughput of our hydrogen isotope ratio mass spectrometer with only half the sample preparation time. It allows analysis of 60 samples per day, as small as 100 microliters.

Long-term tritium records were analyzed by R. Michel to determine the residence times of water in seven river basins in the United States. Residence times ranged from 20 years for the Potomac River above Point of Rocks, Maryland, to 2 years for the Kissimmee River in Florida.

Tritium analyses of samples from the Gann Glacier in Wyoming have been processed and the presence of tritium spikes in presumably old ice suggest that the ice does not retain its vertical integrity, and downward percolation can occur. However, the ice where the tritium spikes occur is physically different than the surrounding ice, so it may be possible to correct for this problem.

We completed hydrogen and oxygen isotopic analyses of 4500 National Stream Quality Accounting Network (NASQAN) and BENCHMARK samples collected between 1985 and 1988 to determine the seasonal and spatial distribution of stable hydrogen and oxygen isotope ratios of United States surface waters and the processes affecting such variation.

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TITLE: Chemical Models of Natural Systems

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

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

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

PROGRESS: The spring 1991 gas sampling at Yucca Mountain, Nev., constituted the fifth year of gas and isotopic sampling at UZ6S and the neutron logging holes, and the second year of gas and isotopic sampling at the 1,850-ft borehole, UZ6. These new data, and recent analysis of older data during time when the open boreholes are dominated by barometric effects, with attendant gas influx and exhaust, are now permitting new inferences and conclusions to be drawn.

The open-borehole gas compositions appear to consist of a mixture of two end-member gases, air and formation gas. The formation gas in the fractured rocks that constitute the bulk of Yucca Mountain contains less carbon dioxide than the gases from the nonwelded tuffs. This complicates attempts at chemical modeling in the fractured tuffs, because the only rocks from which water samples have so far been obtained are the nonwelded tuffs.

GROUND-WATER CHEMISTRY

A check valve was installed on UZ6 in January 1990 in hope of preventing direct access of atmospheric air to the borehole. The 1991 data show that the CO_2 content of the UZ6 gas is approximately 10 percent greater than in 1990. Given the general invariance of the data from the open boreholes, this represents a significant change, and should be accompanied by a decrease in carbon-14 content. The 1991 isotope data are not available as of this writing.

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

PROJECT NUMBER: NR 81—122

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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: Intergranular porosity in the sand grains forming the skeletal framework of the Cape Cod, Mass., aquifer has been documented by W.W. Wood, T.F. Kraemer, and P.P. Hearn. Laboratory evaluation using air abrasion mill, mercury porosimetry, scanning electron microscope, epifluorescence microscopy, column and batch solute tests, and X-ray diffraction support the presences of intergranular porosity and solute diffusion in the interior of grains.

Documentation of the presence of intergranular porosity is consistent with the hydrodynamic dispersivity observed in a large scale solute tracer test on Cape Cod and provides new insight into mechanisms controlling solute transport in clastic aquifer systems. These observation may have important application in aquifer restoration studies in sand and gravel aquifers.
A study by W.W. Wood and W.E. Sanford of Double Lakes, a topographically closed basin near Tahoka, Tex., has identified a significant chemical flux leaving the basin. Diffusion and advection have been identified at this location as the mechanism by which solutes are escaping to the underlying aquifer. Documenting these transport mechanism is consistent with a hypothesis in a paper by Wood and Sanford which proposes that leakage from basins controls the thickness and suite of evaporite minerals formed in an evaporating lake. Work at Double Lakes is on schedule, piezometers have been leveled, all logs, water level measurements and

solute data have been entered into a data management file. Wells have been installed to evaluate the chemical osmotic potential of the underlying shale. Geochemical studies have suggested that eolian transport of evaporite salts from the lake basin to the surrounding area and subsequent leaching from the surface may be responsible for the large ground water solute plume observed down gradient from the lake.

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TITLE: Comparative Study of Organic Degradation in Selected Hydrogeologic Environments

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

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

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

PROGRESS: Field investigations were conducted in shallow aquifers contaminated with hydrocarbons from crude oil or gasoline. The volatile organic compounds dissolved in ground water were isolated and separated by gas chromatography and gas chromatography/mass spectrometry. In the C—6 to C—10 range, 40 organic compounds were identified. The distribution of these compounds in the aquifer can be explained by the hydrogeology and by geochemical processes. Laboratory experiments with microcosms confirm that specific monoaromatic hydrocarbons are degraded anaerobically. Organic acids that were not original components of the oil were identified in the microcosms and at the field sites in the anoxic ground water. These acids were structurally related to alkylbenzenes which suggests that biological transformations of benzene and alkylbenzenes to organic acid intermediates had occurred. The microbial degradation of hydrocarbons in ground water alters the aqueous geochemistry and mineral equilibria of the aquifer. From mass balance calculations, the predominant reactions in an anaerobic plume were organic degradation, dissolution and precipitation of iron minerals, and outgassing of carbon dioxide and methane. Silica and carbonate minerals were dissolved and precipitated, iron oxides were dissolved and an iron carbonate was precipitated.

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

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

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

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

PROGRESS: Determined that Pliocence liqnites may be the source of organic compounds contributing to Balkan Endemic Nephropathy (BEN) in Yugoslavia, Bulgaria, and Romania. Aniline and polycyclic aromatic hydrocarbons seem the most likely compounds to be implicated in BEN. Work with Dr. Philip Hall (Nephrologist, Case Western Reserve University, Cleveland, Ohio) and Dave Wolf (National Mapping Division) indicates that there are restricted geographic areas in the U.S.A. with kidney mortality from disease patterns similar to BEN.

GROUND-WATER CHEMISTRY

Further work on BEN and other diseases has led to a planning meeting between the U.S. Geological Survey and the national Center for Health Statistics for a possible future project. Further work in the Great Hungarian Plain containing ground water drinking supplies with very high nitrate indicate that there may be an increased incidence of gastric cancer in these areas.

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

PROJECT NUMBER: NR 82—138

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

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

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

PROGRESS: Examination of radium isotopes (228Ra and 226Ra) in lakes has continued with the further sampling of two Finger Lakes, (Cayuga and Seneca). Seasonal "structure" in the water column of Lake Cayuga has been detected, indicated by water masses with differing 228Ra/226Ra activity ratio. These differences in isotopic ratio disappear after fall overturn, indicating homogenization of the lake waters. Efforts are still being made to obtain a reasonable "age" of water in the lake, and tritium analyses have been made to help quantify whether 228Ra diffuses into lake water from bottom sediments, complicating the age determination technique. Laboratory studies have been initiated to measure radon solubility in NaCl solutions and organic liquids. Historical data on NaCl solutions appears to be slightly in error, and the present work will correct it. So far radon solubility has been measured in 0, 1N, and 2N NaCl at 7 degrees, 25 degrees, and 42 degrees Celcius. Alkanes from pentane to tetradecane have been selected for radon solubility measurements because of a near total lack of data and because of their importance in gas and petroleum deposits. It has been found that solubility increases from pentane to octane, then decreases again to tetradecane. The reason for this is not understood at present.

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TITLE: Factors Determining Solute Transfer in the Unsaturated Zone

PROJECT NUMBER: WR 68—036

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PROBLEM: Quality of ground and surface waters often is influenced significantly by chemical and solute-dispersion processes of the unsaturated zone. Frequently, these influences are impossible to predict because the effects of certain relevant, unsaturated-zone factors (for example, changes in water content or in the nature of solid surfaces) are understood imperfectly and because the current transport-modeling methods may not be well adapted to the situations encountered in practice. As a result, it may be impossible to assess properly the availability 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: Continued studies of the release of polychlorinated biphenyls (PCB) from sediments in the Lower Fox River in Wisconsin (in cooperation with John Elder, Wisconsin

District). Distribution of PCB between water and sediment phases has been studied in the laboratory using short, saturated, flow-through columns at a variety of water flow rates. Distribution coefficients are similar to previously reported values and the distribution between phases appears to be equilibrium controlled and is not affected by flow rate. Sediment samples from three depths at two sites have been studied using one PCB congener and native river water. Carbon-14 labeled PCB is used to facilitate analyses.

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GROUND-WATER CHEMISTRY

TITLE: Partitioning of Solutes between Solid and Aqueous Phases

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

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

APPROACH: (1) Conduct experiments in the laboratory 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 spectroscopic study of arsenate contamination associated with iron hydroxide precipitates was completed at the Stanford Linear Accelerator Center. The study showed that extremely high concentrations of As can become associated with such precipitates via complexation with surface functional groups. Molar ratios of 0.6 As:Fe were observed in the coprecipitates, but no substitution in the local mineral structure was indicated from the Extended X-ray Absorption Spectroscopy. This is possible because of the extremely small particle size and large surface area of the precipitates. A study of the spatial variability of geochemical and hydrologic parameters in the shallow aquifer at the Toxic Substances Hydrology Research site on Cape Cod, Mass., was begun. The transport of chromium(VI) anions in both oxic and anoxic zones of the aquifer is affected significantly by oxidation-reduction reactions. Reduction was observed in batch experiments with subsurface material from the oxic zone immediately after core collection; dried material lost its reductive capacity.

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GROUND-WATER CHEMISTRY

TITLE: Stable Isotope Tracers of Biogeochemical and Hydrologic Processes

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

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

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

PROGRESS: As part of a collaborative study of stormflow generation in an artificial catchment in China, we have found that the combination of macropore and matrix flow in these silty loams causes up to 5 permil variation in the $\delta^{18}O$ value of soil and groundwater during a storm event. Thus, in small catchments (like WEBB sites) where hillslope waters are a significant component of streamflow, conventional 2-source mixing models may be unsatisfactory. At the Missori Management System Evaluation Area (MSEA) site, we have developed a prototype field method for concentrating nitrate on disposable ion exchange columns for later elution and analysis for nitrogen isotopes. The technique allows us to collect more dilute samples than previously possible, samples will have a much longer shelf-life before analysis is required, and samples will be more easily prepared and analyzed on the automated mass spectrometer. At the Panola watershed in Georgia, we have determined that although rain water intercepted by trees is significantly enriched isotopically compared with nonintercepted rain, the throughfall samples still plot along the local meteoric water line. This suggests that these samples have re-exchanged with local atmospheric vapor subsequent to evaporation, a process that masks the original evaporative pattern. At Lakes Nyos and Monoun in Cameroon, we have determined that the concentrations of dissolved carbon dioxide and methane are increasing with time. The isotopic composition of the carbon dioxide indicates a mantle origin; the methane is biogenic.

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TITLE:	Chemical Modeling and Thermodynamic Data Evaluation of Major and Trace Elements in Acid Mine Waters and Ground Waters
PROJECT NUMBER:	WR 75—128
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PROBLEM: Aqueous chemical models have become popular tools for the interpretations of natural water chemistry. Unfortunately, these models have deficiencies because of (1) incorrect or inconsistent thermodynamic data, (2) invalid assumptions regarding the equilibrium state, (3) inappropriate or unvalidated corrections for nonideality, (4) inadequate expressions for temperature dependence, (5) unvalidated limitations for ionic strength, composition and temperature, and (6) lack of data on solid solution solubility. The plethora of models and databases has prompted federal agencies, especially hazardous waste and nuclear waste managers, to request geochemical code validation. Acid mine waters are a major source of water pollution and provide one of the best challenges to the application of trace element speciation models.

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

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

PROGRESS: (1) Chemical modeling results from participation in the International Pocos de Caldas Natural Analogue Project have been written up and is now in review. These results show the importance of chemical modeling to the use of natural analogues in the management of radioactive waste. (2) Quantitative chemical modeling on ground waters from the International Stripa Project (a radioactive waste research project) has begun. (3) The most extreme example known of acid mine waters has been observed at Iron Mountain, Calif., a Superfund Site for which the project chief is a key advisor. The waters and minerals have been sampled, analyzed and interpreted in an administrative report. These waters have proven to be a major challenge to model and interpret. Values of pH range from 0.5 to —2.0 or less. A second sampling trip, lab measurements and an initial paper are in progress. (4) A major revision of an already-approved report updating the WATEQ4F program has been accepted and is now available for users and for U.S. Geological Survey training courses. (5) A major report on a comparison of techniques for the determination of major and trace elements in acid mine waters has been reviewed and is now being revised.

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TITLE: Geochemistry of Water in Fine Grained Sediments

PROJECT NUMBER: WR 76—139

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

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

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

PROGRESS: Most of the project's effort was devoted to completing the field work and the reports on geochemical investigations of hydraulic connections between the Corwin Springs Known Geothermal Resources Area and adjacent areas of Yellowstone National Park. Two additional field trips were carried out to complete the data coverage in the Norris—Mammoth Corridor of the Park. I coordinated the geochemical aspects of this congressionally mandated study that involved scientists from three Survey projects and several non U.S. Geological Survey geochemists. An extensive geochemical data set consisting of detailed chemical and isotopic compositions of water, solutes, gases and rocks was obtained in order to understand the origins and evolutions of waters in the area. Results are conclusive and show that waters from the Mammoth Hot Springs and La Duke Spring area have evolved chemically and isotopically by reactions with different rock types and are not directly connected. The geochemical data in general, and 3He/4He ratios in particular indicate that the Mammoth system is not directly connected to the Yellowstone caldera but may result from recent magmatic intrusions underneath Mammoth. We have started data analyses on our experiments on water-oil interactions. Results show the generation of reactive organic acid anions directly from crude oils. We have made additional modifications to SOLMINEQ, especially those dealing with treating solutions with high salinity and pH similar to those obtained from reacting brines from Paradox Valley, Colo., (Bureau of Reclamation study) with portlandite and other cements. During this year, project personnel have authored or coauthored four published reports, and one manuscript is in press. I (with H. Barnes) solicited and edited a two-issue volume of Applied Geochemistry devoted to the memory of Ivan Barnes.

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

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

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

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

PROGRESS: Studies of the geochemical evidence for or against a connection between thermal springs in Yellowstone National Park (Mammoth) and adjacent areas outside the park were completed. All sites sampled the previous year were resampled and the waters and gases analyzed. Additional sites were sampled for He-3 and other noble gas isotopes. Isotopic compositions of the noble gases were the most diagnostic indicators of a lack of connection between thermal systems inside and outside the park. No geochemical evidence of a connection was found, and no more than a few percent Mammoth type water could be present in the thermal waters outside the park. Stable isotope data for cold springs collected to determine possible recharge areas for the geothermal waters do not show the typical decrease in heavy isotopes with increasing elevation. The observed enrichment in heavy isotopes with increasing elevation may be attributed to the time of year when the cold springs were sampled (August) and to the large number of late summer thunder showers over the highlands. Disordered dolomite has been synthesized and the isotope fractionation factors between the synthetic carbonate and water have been determined for oxygen and carbon between 25 and 80 degrees Celsius. Experimental results have been repeated by separate syntheses and isotope fraction factor determinations. The structural state of the disordered "dolomite" has been determined by X-ray diffraction techniques.

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GROUND-WATER CHEMISTRY

TITLE: Chemistry of Aquatic Organic Matter

PROJECT NUMBER: WR 84–189

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

OBJECTIVE: (1) Identify organic substances associated with a given field problem, in aqueous and nonaqueous 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: Discovered zones of aerobic alterations, denitrification and sulfate reduction in the creosote contaminated ground water at Pensacola, Fla. The discovery resulted from detailed chemical analyses of water samples from the aerobic-anaerobic transition zone near the open ground-water table. Also, analyzed samples collected from beneath an abandoned creosote works at Jackson, Tenn., in order to compare results to analyses of samples from the Pensacola, Fla., site.

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GROUND-WATER CHEMISTRY

TITLE: Geochemical Reactions Between Water and Mineral Substrates

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

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

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

PROGRESS: Progress continued on investigation of heterogeneous 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 ilmenite surfaces. The surface reaction which controls this electron transfer involves surface dissolution of ferrous iron coupled with solid state transition to a maghemitite structure.

Synthesis of existing data on the role and characterization of reactive surface areas on mineral dissolution also was conducted and laboratory determinations made 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 assuming a direct relationship 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.

Progress continued on characterizing Se distributions in the Central Valley of California both at Kesterson and the Coastal Range source area. Conditions controlling Se release in the latter case include: deep weathering and extensive outcropping of Se-containing marine Tertiary-Cretaceous sediments resulting from the inherently unstable landscape; the oxidation of disseminated pyrite in which alkaline pH conditions are maintained by extensive carbonate buffering capacity, the inherent mobility of selenate, the oxidized form of Se; and finally, the partial incorporation of Se in hydrous sulfate salts in the surface soils. In constract Se immobilization 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. 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 based on release rates of Cl, B, and Li in the case of the Bandelier Tuff which obeyed a generalized Arrhenius rate equation.

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Page 147 follows

GROUND-WATER HYDROLOGY

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

PROJECT NUMBER: CR 74–090

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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 for only a few large reservoirs in the western United States. Many commonly used methods of estimating surface runoff to lakes are inaccurate. Hydrogeologic controls on seepage have not 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 and Shingobee Lake, Minn., and Mirror Lake, N.H., to better define the geologic boundaries of the ground-water flow systems associated with the lakes. Additional water-table wells were constructed at Williams Lake and Shingobee Lake as part of the drilling program to better define the water-table configuration in selected parts of the watersheds. (2) Preliminary analysis of a 10-year data set on ground water interaction with prairie wetlands in North Dakota indicates that flow reversals between these surface water bodies and ground water are extremely common around the entire perimeter of a wetland that was previously thought to be primarily a ground-water discharge feature. (3) To facilitate better understanding of the dynamic changes in ground-water flow systems and related chemistry at the edge of surface-water bodies, additional groups of wells were installed and instrumented with recording temperature and specific conductance sensors at Cottonwood Lake, N. Dak. (4) Analytical work and report writing focused on evaporation studies of Williams Lake, Minn., has resulted in two completed reports, one of which has been approved by the Director. A third report is in progress.

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TITLE: Borehole Geophysics as Applied to Geohydrology

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

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

APPROACH: Log selected drill holes, determining core analyses, 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: A.E. Hess published a symposium proceedings paper documenting the application of flowmeter techniques to several different geohydrologic studies. R.H. Morin published journal articles on fracture permeability characterization using flowmeter logs, and on the interpretation of in situ stress using geophysical logs. F.L. Paillet produced a research monograph on acoustic logging theory and application to geohydrology, a comprehensive review volume on the application of well logging to radioactive waste repository sites, and served as chairman of several professional society committees producing review volumes of position papers on fracture interpretation. F.L. Paillet produced the first dynamic fracture model that successfully relates both attenuation and refraction of borehole tube waves to fracture permeability in situ.

GROUND-WATER HYDROLOGY

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

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

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

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

PROGRESS: (1) The methods for calculating simultaneous posterior (Bayes') confidence intervals for output from ground-water flow models were extended to include an unknown range of possible errors in the output. The unknown error range was considered to be a random variable with a noninformative prior distribution so that the posterior distribution obtained using Bayes' theorem is a distribution of model parameters conditioned on the data used for model calibration. A paper describing the new methods and giving numerical substantiation has been written. (2) Two papers describing the basic methods for computing simultaneous prior and posterior (Bayes') confidence intervals are through colleague review and have been revised for final submission for approval as journal papers. (3) A report detailing the theory and numerical methodology of a preconditioned, conjugate gradient solver for the Modular

Finite-Element Model (MODFE) for ground-water flow simulation was published. (4) A Parameter-Estimation Package that is to be used with a modified version of the three-dimensional, transient, modular, finite-difference ground-water flow model (MODFLOWP) was expanded so that parameterizations may be based on kriging. This allows realistic spatial variations in, for example, hydraulic conductivity, to be represented. (5) Documentation of the Parameter-Estimation Package and MODFLOWP was completed; reviewed by three colleagues and an editor; used by district personnel in Ithaca, N.Y., Eugene, Oreg., and Lansing, Mich., and NRP personnel in Menlo Park; used to teach a class at the National Training Center; revised based on the input from these sources; and submitted to region. (6) A study that considers the impact of inconsistencies between the assumed and actual statistics of errors in dependent-variable observations used to estimate parameters was begun.

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TITLE: Field Applications of Unsaturated Zone Flow Theory

PROJECT NUMBER: CR 69–200

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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) Measurements of evapotranspiration (ET) were made over hilly semiarid rangeland in southern Arizona before and during a monsoon season as part of a multiagency experiment to investigate the use of remotely sensed data to estimate ET in such environments. (2) Data analysis and report preparation continue on the results of a 3-year study of ET from phreatophytic scrubland in the San Luis Valley. (3) Data analysis of air flow through Yucca Mountain continued with the effects of barometric pressure changes, temperature-affected density-induced flow, and wind-generated flow being quantified. (4) Documentation of a finite-difference-based numerical transport code for the simulation of flow and transport in variably saturated media has been published, and is now being widely used both within and outside the U.S. Geological Survey. (5) Field investigations of rapid transport of agricultural chemicals through the unsaturated zone based on macropore flow and preferential flow paths were initiated at Midcontinent Herbicide Initiative field sites in Missouri and in Minnesota. These studies involve the use of air permeability data and gas tracer tests to infer soil structure, as well as more classical lysimeter and core studies. Preliminary air-permeability and gas-tracer experiments have been completed, as have the lysimeter installations.

GROUND-WATER HYDROLOGY

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TITLE: Ground-Water Solute-Transport Simulation

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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: A prototype computer code for simulating multispecies solute transport in one dimension with equilibrium controlled precipitation/dissolution and oxidation/reduction reactions was further refined. It was applied to nitrogen-compound transport at a site in Denmark. A journal article on the model and the application has received Director's approval. A new iterative, linear equation solver was developed based on red-black nodal renumbering and a restarted conjugate gradient method. Sensitivity to renumbering order is being investigated. A computer code was developed to test the use of an implicit pressure equation with an explicit solute transport equation for three-dimensional simulations. A model was developed to characterize the sorption of uranium and molybdate at the Weldon Springs Site Remedial Action Project in cooperation with the Missouri District. Refinement continued of the geochemical reaction-path model for the Pinal Creek site, Arizona. Both project members spent a month reviewing the Hanford Federal Facility Liquid Effluent Study Project reports in cooperation with the Pacific Northwest District at the request of the Environmental Protection Agency. Through the Nuclear Hydrology Program, a one-dimensional multispecies solute transport code was obtained and evaluated for simulation of molybdate in column experiments. Program modifications increased computation speed by a factor of 5.

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TITLE: Application of Stochastic Processes in Hydrogeology

PROJECT NUMBER: CR 90–319

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

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

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

PROGRESS: An analysis of steady, radial flow in heterogeneous porous media has been completed and a report, entitled, "Radial flow in heterogeneous porous media: an analysis of specific discharge," was published in Water Resources Research. Because of the complexity of the analysis, it was necessary to limit the investigation to the first and second moments of the specific discharge. The first moment of specific discharge can be used as a measure of the effective hydraulic conductivity of the medium; the second moment gives one an idea of the goodness of this measure. The first moment suggests that, at reasonable distances from the well, the effective hydraulic conductivity can vary from an arithmetic mean for three dimensional flow in a highly stratified medium to a harmonic mean for two-dimensional flow in an isotropic medium. The variance in specific discharge is basically proportional to the inverse square of the distance from the well.

An investigation of arrival times and breakthrough curves for transport in heterogeneous porous media has been completed. An initial report concerning the breakthrough curves and their moments was published in the Proceedings of International Conference and Workshop on Transport and Mass Exchange Processes in Sand and Gravel Aquifers: Field and Modeling Studies held in Ottawa, Canada, October 1—4, 1990; a full report entitled "Arrival Times and Temporal Moments For An Imperfectly Stratified Aquifer" has been accepted for publication in Water Resources Research. This research has concerned itself with the production of mean breakthrough curves for an instantaneous pulse input of tracer when hydraulic dispersion is the result of flow through heterogeneous porous media, and with the mean arrival time density function of a tracer particle. The breakthrough curves demonstrate very nonFickian behavior in early time, which results from the mechanism by which no concentration flux can be "dispersed" upgradient, as common to a Fickian flux in early time. The arrival time cumulative distribution function allows one to quantify the expected probability of the arrival of a tracer particle at a location in the mean flow direction.

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TITLE: Hydrologic Behavior of Cretaceous Shales

PROJECT NUMBER: NR 81—035

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

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

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

PROGRESS: (1) Much of the past year has been devoted to completing analysis of the Pierre Shale flow system. A good deal of analysis was carried on concurrently with, and as a result of, putting the results in manuscript form. The results include: (a) The erosion that created the underpressures may have been a fairly rapid episode as much as 0.5 Ma ago with little erosion since. In this scenario the shale would have had fluid pressures significantly into the absolute negative range in the past. (b) Identification of a slow increasing trend in measured pressures as probably due to leakage through the cement plug in the boreholes; the cement is 100 times more permeable than the shale. (2) Development of a strategy for identifying geologic sites hydrologically suitable for waste disposal. The strategy is based on the recognition of naturally transient flow regimes. The Pierre Shale work has demonstrated that such regimes can be detected in "pure" low-permeability settings. Such findings offer very strong assurances about the small fluid fluxes in the system and their predictability. (3) A cooperative effort with Warren Wood and Ward Sanford allowed duplication of the earlier Pierre Shale osmosis experiment in a thinner, more permeable shale in Texas. Preliminary results show no evident osmotic effects at the Texas site.

GROUND-WATER HYDROLOGY

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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

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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 measurement techniques, as byproducts of the investigations.

PROGRESS: Optimal network design strategy has been successfully tested on the field-scale tracer test at Otis Air Force Base, Cape Cod, Mass., and has demonstrated the value of employing simple models of transport on sparse data sets. Variable-density flow and solute transport simulation analysis of the transition zone in the major coastal aquifer in Oahu, Hawaii, has resulted in identification of major processes controlling regional transition zone dynamics. Field measurements in Oahu, Hawaii, to determine scale effects in hydraulic and transport behavior of structured heterogeneous aquifers are complete and isotopic and chemical analysis is underway. Evaluation of data on ground-water flow in crystalline basement rocks in Sweden is underway.

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TITLE: Digital Modeling of Transport in the Saturated Zone

PROJECT NUMBER: NR 81—120

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PROBLEM: Management of ground-water resources requires that the extent and rate of movement of contaminants in the saturated and unsaturated zones be understood. Contaminants have been and will continue to be 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 tested and documented.

OBJECTIVE: Investigate the parameters in basic mathematical transport models developed for ground-water systems to increase understanding of the factors influencing these parameters and of the interrelation between parameters. Derive appropriate two- and three-dimensional mathematical models to describe contaminant movement in complex field situations, 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: An analysis of the effects of transient flow on apparent dispersion in ground water has been completed. Ignored or unknown transients in the direction of flow primarily act to increase the apparent transverse dispersivity because the longitudinal dispersivity is acting in a direction that is not the assumed flow direction. The effects of neglecting transient flow has only a small effect on the apparent longitudinal dispersivity. A preliminary working version of a solute-transport module for the MODFLOW ground-water flow model has been developed. The module is based on an extension of a two-dimensional method-of-characteristics model. Investigations have continued at a saline lake on the Southern High Plains of West Texas. Water levels and geochemical evidence indicate solutes from water in the lake sediments are moving via ground water downward into a confined limestone aquifer but not horizontally into the surficial Ogallala aquifer. Further evidence indicates that eolian activity is responsible for the high solute concentration in the Ogallala aquifer. Wind is moving salt crystals from the dry lake bed to the surrounding land surface, where recharge carries the salts downward into the aquifer. A theoretical analysis of the behavior of hydrologically open saline lake systems has indicated that the type and amounts of minerals deposited in such lake basins are a strong function of the amount of leakage from such basins. An article was published in Economic Geology describing the behavior of open lake systems in continental environments. A second article predicting the effects of leakage on an open basin with seawater has been accepted for publication by the American Journal of Science. A numerical modeling study of the ground-water system around Poas Volcano in Costa Rica has indicated that hot, acidic, brine from the active crater lake is migrating to acid springs on the northwest flank of the volcano in a period of less than 10 years. These results are in general agreement with temporal studies by other scientists that have been done of the crater lake and spring water chemistry.

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GROUND-WATER HYDROLOGY

TITLE: Multivariate Statistical Techniques for Assessing Regional Ground-Water Quality and Quantity

PROJECT NUMBER: NR 84—130

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

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

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

PROGRESS: Present work activities are related to the overall objectives of National Water Quality Assessment (NAWQA) Program to characterize the Nation's Ground and Surface waters. Water-Quality data have been compiled into a data set and summary statistics for key chemical variables have been studied. Multivariate statistical methods are being used in a variety of modes to assess the chemical character of ground waters in aquifers. Cluster analysis and other multivariate methods are key methods in understanding ground-water quality in study area. A report has been published on the radon content of geologic units in the Coastal

Plain and Piedmont physiographic provinces that presents a new ranking system of those geologic units and their potential to contain radon.

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TITLE: Transport Phenomena in Fractured Rock

PROJECT NUMBER: NR 84—134

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

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

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

PROGRESS: A multidisciplinary investigation to develop field techniques and interpretive methods of characterizing and predicting fluid movement and chemical transport in fractured rock was organized in cooperation with the New England District Office of the Water Resources Division, Geologic Division, and five other research projects in the National Research Program in the Water Resources Division. The field investigations are being conducted in the Mirror Lake drainage basin in the Hubbard Brook Experimental Forest in central New Hampshire. These investigations couple geologic and fracture mapping, surface- and borehole-geophysics, ground-water geochemistry, hydraulic and tracer testing, and ground-water and solute-transport modelling. Hydraulic tests to identify the variability of hydraulic properties of the bedrock were conducted as this research project's part in the multidisciplinary investigation. The results of these hydraulic tests were used to develop preliminary conceptual models of the heterogeneous hydraulic properties of the bedrock in the

Mirror Lake drainage basin that will be used in subsequent modeling efforts. Conceptual advances in using a stochastic description of hydraulic properties to predict solute transport in heterogeneous subsurface environments also were made. A three-dimensional description of the solute flux was developed; previous work considered only a one-dimensional description of the solute flux in heterogeneous subsurface environments. The methodology used in this analysis also allowed for higher-order perturbation approximations to be investigated in the description of solute transport in heterogeneous subsurface environments; in previous investigations, only first-order perturbation approximations were considered. These advances will allow investigations of the robustness of the first-order perturbation approximations and the impact of larger variability in the hydraulic properties of the subsurface.

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GROUND-WATER HYDROLOGY

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

PROJECT NUMBER: NR 73—139

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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.

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

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

PROJECT NUMBER: WR 63–024

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

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

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

PROGRESS: In collaboration with H. Gvirtzman (Weizmann Institute), Pacific Northwest District personnel, and other National Research Projects, field and laboratory studies were conducted on unsaturated water movement in several settings having deep, unsaturated zones. A previously developed cryo-distillation method was tested for its degree of induced isotopic fractionation and found to be free, for the materials considered, of significant induced shifts in oxygen-18 and deuterium levels. Values of these two isotopes in water samples that were extracted from a deep unsaturated profile in eastern Washington state showed significant correlation, departed strongly from the meteoric water line, and varied in magnitude by amounts consistent with present-day meteoric fluctuations. Results also showed that fractionation is confined to the shallow subsurface, and that values from deep unsaturated zones may reliably indicate climate change. In collaboration with the Unsaturated Zone Flow Project (WR198), predictions of theoretical models that relate hydraulic conductivity to water content were tested using data obtained on core samples from an alluvial fan in western Fresno County, Calif. In collaboration with the Non-Isothermal Multiphase Flow Project (WR179), a down-bore time-domain-reflectometry probe previously developed for rapid determination of water-content profiles was used to make measurements on samples brought to known bulk densities and water contents in the laboratory; these measurements were used to test a theoretical model relating the dielectric properties of a composite material to the volume fractions and dielectric constants of its constituents.

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

Nimmo, J.R., and Miller, E.E., 1986, The temperature dependence of isothermal moisture-vs.-potential characteristics of soils: Soil Science Society of America Journal, v. 50, p. 1105—1113.

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

PROJECT NUMBER: WR 73—102

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

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

APPROACH: Collect and synthesize geologic, geophysical, geochemical, and hydrologic data, including data obtainable from drill holes, for specific geothermal systems at Long Valley caldera (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: A multidiscipline study of the effects of geothermal development in the Corwin Springs KGRA on thermal features in Yellowstone National Park was completed and a Water-Resources Investigation report written and approved. This report provides the basis for Congressional action to limit geothermal development outside the Park. In the Long Valley caldera, Calif., additional data on changes in helium isotopic content of fumarolic gas from Mammoth Mountain provides further support for the conclusion that magmatic intrusion accompanied the onset of seismic activity beneath the mountain in 1989. Similar isotopic changes in fumarolic gas were not found in other parts of the caldera that also have experienced episodes of increased seismic activity. A journal article on new evidence for source of hot water in the Long Valley hydrothermal system was accepted for publication in a special issue of Journal of Volcanology and Geothermal Research.

REPORTS PUBLISHED 1986—1991:

Farrar, C.D., Sorey, M.L., Rojstaczer, S.A., and Steinemann, A.C., 1989: U.S. Geological Survey Water-Resources Investigations Report 89—4033, 70 p.

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TITLE: Technical Coordination and Support of WRD Geothermal Studies

PROJECT NUMBER: WR 72–108

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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 necessary 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.

TITLE: Hydrologic Studies of Heat and Mass Transport

PROJECT NUMBER: WR 74–121

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

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

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

PROGRESS: Completed Professional Paper 1044–L, which describes heat flow and hydrothermal circulation in the north-central Oregon Cascade Range. This section of the Cascade Range volcanic arc is characterized by relatively high Quaternary volcanic extrusion rates and hot-spring discharge rates, and by high conductive heat flow. However, a large area of near-zero near-surface conductive heat flow occurs in the younger volcanic rocks, due to downward and lateral flow of cold groundwater. Alternate models for the high heat flow observed in older rocks on the flanks of the Cascade Range include (1) a laterally extensive midcrustal heat source or (2) a narrower, spottier deep heat source flanked by relatively shallow conductive heat-flow anomalies caused by regional ground-water flow. We simulated ground-water flow and heat transport through two cross sections west of the Cascade Range crest. Measured temperature profiles, hot-spring discharge rates, and geochemical inferences constrain the results. The numerical simulations provide some estimates of regional-scale permeabilities; simulated bulk permeabilities of approximately 10^{-14} m^2 in the youngest (0—2.3 m.y.) rocks and approximately 10^{-17} m^2 in the oldest (18—25 m.y.) rocks allow the thermal observations to be matched. In the simulations, the alternate conceptual models for the deep thermal structure were represented as wide or localized deep heat sources. We found that either model can satisfy the observations. A program of stream sampling in the Lassen area, northern California, suggests that the mass ratio of liquid outflow to steam upflow (approximately 40 kg/s; Sorey and Simpson, 1991) from the Lassen hydrothermal system is less than 1:1, whereas Ingebritsen and Sorey's (WRR, 1985) numerical simulations of the Lassen hydrothermal system led to liquid:steam discharge ratios on the order of 10:1. Modifications to their model to allow much lower liquid:steam ratios might involve recirculation and reheating of high-chloride water and/or long-term transient response to magmatic heat input or permeability changes. Modifications to Bodvarsson's (1982) PT code allow simulation of relatively high-temperature (up to 1,000°C) single-phase systems. The improved model is being applied to the Skaergaard system, East Greenland.

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Ingebritsen, S.E., Carothers, W.W., Mariner, R.H., Gudmundsson, J.S., and Sammel, E.A., 1986, Flow testing of the Newberry 2 research drillhole, Newberry Volcano, Oregon: U.S. Geological Survey Water-Resources Investigations Report 86—4133, 23 p.

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TITLE: Analytical Modeling of Flow and Transport in Aquifers and Geothermal Reservoirs.

PROJECT NUMBER: WR 75—127

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

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

APPROACH: Controlling equations for flow and transport in porous and fractured-rock aquifers are modified, linearized and solved with appropriate boundary conditions. For complex systems, the approach often involves the use of integral transforms and special methods of numerical inversion. Finite-difference or finite-element computer codes and laboratory data may be used to check the results. Field data are used for case studies.

PROGRESS: Improvements have been made in the analytical model for convergent radial dispersion (Water Resources Research, March, 1989) by applying a new Laplace transform inversion algorithm that not only speeds up computation but also allows for generation of type curves for large Peclet numbers. A paper describing the improvements has been submitted to Water Resources Research for possible publication. A convergent-flow tracer test was conducted simultaneous with a long term pump test in a sand and gravel aquifer, Cape Cod, Mass. The idea was to test the hypothesis that tracer diffuses into the porous grains of the aquifer. This was to be accomplished by applying the model for convergent radial dispersion, which had been modified to account for the phenomenon. Results were inconclusive and additional tests are planned. Some minor improvements have been made on a well-hydraulics model for flow to a partially penetrating well in a double-porosity, water-table aquifer.

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TITLE: Hydrologic Analysis of Petrofabrics--Sandstones

PROJECT NUMBER: WR 76—171

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

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

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

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

TITLE: Water Wells as Strain Meters

PROJECT NUMBER: WR 75—176

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

OBJECTIVE: 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.

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

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TITLE: Models for Ground-Water Management

PROJECT NUMBER: WR 82—178

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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: Results of the field investigation of a hypothetical water rental market in southeastern Colorado showed the benefit to farmers and were published in Water Resources Research. In addition, a new optimization method for aquifer remediation, which considers spatial variability of hydraulic conductivity, was developed and illustrated in a new publication. The computer code AQMAN was converted for common use on a personal computer. Finally, a preliminary model of the hydrogeology of Santa Clara Valley, Calif., was completed.

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TITLE:	Nonisothermal Multiphase Flow
PROJECT NUMBER:	WR 82—179
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PROBLEM: Understanding multiphase fluid flow in the subsurface is of increasing importance. Large volumes of organic liquids which are not miscible with water (such as gasoline) are being introduced into ground-water systems from leaking storage tanks. Such fluids have become a major source of ground-water contamination. Understanding how immiscible fluids move in the ground, and how they interact with the sediment, the soil gas, and the ground water, is vital to protecting the nation's water supply. Information on 3-phase flow is available in the petroleum engineering literature, but much of this work is not applicable because capillary pressure effects, which are important in small-scale, near-surface ground-water systems, have generally been ignored.

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

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

PROGRESS: W.N. Herkelrath, in collaboration with H.I. Essaid and K.M. Hess, carried out field investigations of multiphase, immiscible flow of fluids in sediments. As part of an effort to gain insight into the processes controlling the movement of immiscible contaminants in the field, a method was developed for determining the spatial distribution of water, air, and immiscible fluid saturation within a polluted ground-water system. The method involves obtaining undisturbed sediment cores from the field with fluids intact, and then analyzing the core in the laboratory to determine fluid saturations. The method was tested at the site of a large oil spill near Bemidji, Minn. Analysis of the results indicates that 11 years after the oil spill, the oil saturation in the sediments is still high, and the oil continues to spread laterally in the aquifer. The oil distribution is complex and appears to be strongly influenced by heterogeneity in the sediment profile. The thickness of oil in wells was a poor indicator of the measured distribution of oil in the subsurface. Saturation data were used to test a cross-sectional, multiphase numerical flow model. The saturation distribution simulated assuming uniform mean properties was a poor match to the observed distribution. Better agreement was achieved when representations of observed spatial variability were incorporated into the model. However, more data are needed to better estimate the retention and relative permeability functions and to better characterize the correlation structure of the sediment properties. Work continued on developing laboratory methods for measuring two- and three-phase (hysteretic) capillary pressure and relative permeability relationships for sediment cores. Experiments using uniformly packed sand cores showed that a simple surface-tension scaling model does a good job in predicting the two-phase (oil/water) initial-drainage curve; however, the measured pressure-saturation hysteresis loops diverged significantly from model predictions.

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

PROJECT NUMBER: WR 82—180

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

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

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

PROGRESS: Feed-Forward (FF) method derives efficient operational equations for simulating solute transport problems with equilibrium-controlled reaction networks. Using sequential, network-type by network-type and also theoretical approaches, completed the removal of this method's limitation, restricting its applicability to reaction-segments with three participants which are at most binary. An algebraic, matrix-rank procedure has been adapted and augmented to serve as an easy-to-use method for testing solvability of postulated reaction-systems. Established certain necessary conditions for solvability which can help in formulation of reaction networks to be simulated. As a part of a program of constructing a broadly applicable, FF-method based, solute transport code, devised and successfully employed FF-method's algorithms for simulating transport with the following networks: one with a three segment network in which all the main reaction classes are represented; ones with precipitation and aqueous complexation networks of any size and shape; and one with a ribbon-shaped network of ion-exchange reaction segments. Started expressing the FF-method in terms of matrix algebra to assist in modularization of transport algorithms. Developed a new approach to modelling transport problems which may involve all classes of chemical reactions, both kinetics and equilibrium controlled. The approach uses methods of linear vector spaces and defines reaction coordinates for the problems based on the reaction stoichiometry. Since the resulting equations isolate each chemical reaction expression into a single equation, this approach appears to be ideal for treating problems in which some reactions are in equilibrium and others are kinetically controlled. The resulting equations are compact in form and have potential use as the basis of a general simulation code. The method has been tested on a number of relatively elementary one-dimensional simulation examples.

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TITLE: Hydrology of Fractured Rocks

PROJECT NUMBER: WR 83—184

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

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

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

PROGRESS: Field work continues at the research site at the Mirror Lake drainage basin near West Thornton, N.H. Field activities during the summer and fall of 1990 included well drilling, packer tests and water sample collection at various depths in bedrock wells, and long-term monitoring of water level fluctuations. Preliminary analysis of field data suggests that: (1) an active ground-water flow system exists in the bedrock of the Mirror Lake drainage basin, (2) the bedrock is highly heterogeneous, with fractures and hydraulic properties strongly controlled by lithology, (3) despite the heterogeneities, overall water movement can be simulated by conventional ground-water modeling techniques, but (4) distribution of solute concentration may be highly irregular and a stochastic approach may be required to model transport process. A computer model was developed to simulate steady-state drawdown due to pumping a well in the vicinity of a high-permeability fracture zone. This model is intended to be used with parameter-estimation techniques for analyzing hydraulic tests in heterogeneous fractured rocks.

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TITLE: Temperature Effects in the Unsaturated Zone

PROJECT NUMBER: WR 87–193

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

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

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

PROGRESS: I published a paper based on a series of isothermal-isobaric water retention experiments to examine path-dependence during water desorption in porous materials. An understanding of the relation between pore-water pressure and temperature is essential for accurately modeling the effects of low-temperature geothermal, high-level nuclear hydrology, and global changes (e.g., warmer climates) on water retention and flow processes that occur in the unsaturated zone.

REPORTS PUBLISHED 1987—1991:

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TITLE: Physical Characteristics that Determine Flow in the Unsaturated Zone

PROJECT NUMBER: WR 89—198

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

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

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

PROGRESS: (1) Several models predicting unsaturated hydraulic conductivity (K) were investigated using measurements of low-water-content soil moisture characteristics previously made by this project on deep-unsaturated-zone core samples from a site in the San Joaquin Valley, Calif. The results show (a) that currently available models poorly predict K for samples and conditions of this type and (b) that capillary-based models fit the data somewhat better than a new fractal-surface model intended for low water contents. (2) A method and apparatus were developed to simultaneously measure total compressive strain and saturated K of soil core samples in a centrifuge. Initial results show that elastic compression may have caused anomalies noted in earlier attempts to measure K for samples from a site in southeastern Washington. (3) An improved version of C.D. Ripple's soil-packing machine was completed, in a collaboration with project WR—024. Tests show the basic performance of this machine to equal that of Ripple's machine, while it is superior in versatility, portability, and ease of use. (4) Initial soil core sampling at a hazardous waste site at the Idaho National Engineering Laboratory (INEL) has shown (a) that the near-surface medium should be suitable for ordinary core sampling methods as long as the soil is wet enough for adequate cohesion, and (b) that there are significant variations in soil penetrability consistent with different previous soil treatments. (5) Continuing developments of the steady-state centrifuge method (SSCM) for measuring unsaturated hydraulic conductivity included (a) a partly successful attempt to measure K of consolidated media, and (b) the design and construction of a modified flow-controlling device that should permit operation at lower K values and for a greater variety of media.

REPORTS PUBLISHED 1989—1991:

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

PROJECT NUMBER: WR 89—199

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

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

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

PROGRESS: A study of flow in layered coastal aquifer systems has been completed. This work has resulted in a better understanding of the coupled behavior of freshwater and saltwater flow under transient conditions, and interface movement in complex coastal aquifer systems. As part of this study, a computer model (SHARP) has been written and documented. The model and an application to the Soquel-Aptos Basin, Calif., has been published in a journal article. Research involving the transport of immiscible organic contaminants is underway. A method for determining field air, oil and water saturations has been applied at the Bemidji, Minn., toxic water research site. This field effort has provided data sets for testing of a two-dimensional numerical model of air, oil and water flow. The model incorporates hysteresis and oil entrapment, and allows for distributed parameters. It is being used to study the level of characterization of sediment properties needed, and the complexity of processes which must be incorporated into the model to successfully simulate the behavior of an oil spill under field conditions. Geostatistical representations of observed heterogeneity at the site are being used to study the influence of variability in sediment properties on oil lens movement and distribution in the subsurface. Monte Carlo simulations of a hypothetical oil lens indicate that the subsurface oil distribution is more sensitive to variability in the shape of the retention curve than variability in permeability. The results this effort have been presented at seminars at the University of Wisconsin, Madison, (September 1990) and the Oregon Graduate Center (October 1990), at the U.S. Environmental Protection Agency's San Francisco office (March 1991), and at the U.S. Geological Survey Toxic Substances Hydrology Program Technical Meeting (March 1991).

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SURFACE-WATER CHEMISTRY

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

PROJECT NUMBER: CR 68—046

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

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

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

PROGRESS: The organic samples from the control and the "to be acidified" watersheds in the Norway Humex acid rain study are the same according to data from H—NMR analysis, ^{13}C—NMR analysis, amino acid analysis, protonation analysis, and elemental analysis. Because the waters from the watersheds are chemically the same, potential future differences due to acidification of one of the watersheds may be established. The analyses of humic samples from surface and ground waters collected in England are continuing. Preliminary results indicate that the composition of stream humic substances are greatly influenced by soil blanket peats. This finding is contrary to numerous other studies in which stream humic substances are different from soil humic substances. Mutagenic and carcinogen studies on the chlorination of humic substances from waters in England are being conducted by Ames tests, profuse liver enzyme cultures, and various cell cultures. The low-molecular-weight organic acids rather than the humic acids produce the highest mutagenic effects.

Studies to quantify ^{13}C—NMR spectral analyses are continuing. The variable contact time experiments for solid-state ^{13}C—NMR indicate that only semi-quantitative analyses can be achieved at a specific contact time of 1 ms. For quantitative results on carbon types in a given humic acid sample, a variable contact time experiment must be conducted. The TCH and T1p time constants are nonhomogeneous for carbon types within each humic substance. The most variable time constants are for peat humic substances.

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TITLE: Behavior of Natural Polyelectrolytes in Water

PROJECT NUMBER: CR 68–132

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

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

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

^{14}N and ^{15}N NMR spectra of humic isolates; (8) isolate and identify carbohydrates from soil and compost extracts; (9) characterize by ^{13}C NMR spectroscopy humic substances isolated from water treatment plants and composts.

PROGRESS: (1) A study on the identification of a polysaccharide fraction isolated from an agricultural soil from the Philippines has been completed. We have shown that the major polysaccharide component is a dextran (1,6 linked glucose units). Other polysaccharide components were identified as well. This is the first time that polysaccharides have been isolated and identified from soils. (2) The first phase of a study on the origin of colored waters in wells near the site of trichlorethylene (TCE) contamination at the Picatinny Arsenal, New Jersey, has been completed. We have shown that the colored water is most probably soil pore water that has been displaced downward by TCE which has a higher density than water. (3) A collaborative study of the leachate from the composting of leaves has been undertaken with Robert Melvin from the New England District. This study is being carried out near Hartford, Connecticut. Leachate will be collected by lysimeters installed at two depths beneath a compost winrow. In addition, the liquid in the compost itself will be sampled. The composition of the organic compounds in the leachates collected by the lysimeters will be compared with composition of the organic compounds in the compost solution in order to determine what types of compounds are being sorbed by the soil minerals. (4) A report has been completed on the humification process. In this report a new model of the humification process is presented. Data from all of the studies that we carried out over the last 25 years, and data from the literature have been used in developing the model. (5) The first phase of a study on the fixation of ammonia by humic substances has been completed. In this study ^{15}N labelled ammonia was reacted with the humic substances, and the products were analyses by ^{15}N and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. A journal report on this work has received Director's approval and has been submitted for publication. (6) A study has been started in collaboration with M.A. Mikita at California State University in Bakersfield on chemodenitrification mediated by humic substances. Initial results of this work have been reported at the Environmental Analytical Chemistry symposium of the Pittsburgh Conference as a featured, invited paper. This work has resulted in M.A. Mikita being awarded two competitive grants to continue this research. (7) A research project has been initiated with E.J. Weber of the Environmental Protection Agency (EPA) on the covalent binding of aniline compounds by humic substances. Initial results were reported at the 5th International Humic Substances Society meeting, Nagoya, Japan. A research proposal to continue this work was funded by an EPA 2 percent set-aside competition grant for innovative research. Only four out of fifty or more proposals were funded in this competition. (8) A collaborative research project with John Hem and David Vivid of WRD, Menlo Park, on the speciation of aluminum in hydroxy-aluminum solutions by ^{27}Al NMR has been initiated. (9) A method has been developed for the isolation of hydrophilic organic acids from aquatic environments using sorption on nonionic macroreticular resins. A report has been prepared and has been submitted for publication. (10) Three fractions of nonvolatile organic acids resulting from the biodegradation crude oil have been isolated from a well downgradient of a crude oil spill at Bemidji, Minn. The organic acids and the undegraded crude oil have been characterized by ^{13}C NMR spectroscopy. In addition, ^{14}C age dates have been measured on the organic acids; these data are being used to determine the sources of the acids and the degree of mixing of the acids from the crude oil with the native dissolved organic substances. (11) The fourth year of field work on Lake Frywell in the Dry Valleys of Antarctica has been completed. Organic acids from an inflow stream and from the moat around the lake have been isolated. These samples are now being analyzed. Seasonal dissolved organic carbon inputs to the lake were determined by sampling 10 streams during the Austral summer. In addition, sediment cores were collected from the lake, and are presently being analyzed. Two reports on this work have been accepted for publication. (12) Intensive dissolved organic carbon (DOC) sampling combined with ultraviolet absorption measurements of Williams and Shingabee Lakes (Integrated Research Initiative sites) are being used to determine the effect of DOC on light attenuation in lakes. Preliminary ^{13}C NMR results indicate that allochthonous DOC derived from soils has higher aromaticity and greater light absorbance than autochthonous DOC. (13) A study of the significance and nature of chloride interference on dissolved organic carbon analyses by the persulfate oxidation method has been completed. Results will be written up for publication.

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TITLE: Geochemical Kinetics Studies of Silicate Rock Hydrologic Systems

PROJECT NUMBER: CR 75—189

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

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

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

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

II. Dry-deposition studies in the American Monsoonal region of southern Arizona have made progress. Micrometeorological flux measurements should begin in Fiscal Year 1992, as 95 percent of the hardware has been purchased, the meteorological tower has been installed and cooperation from the National Park Service has been obtained. This study is a multidisciplinary study involving Universities and other Federal Agencies in addition to WRD. The objectives include: (1) determination of dry flux inputs that are of geologic/hydrologic interest, specifically Ca and Cl, (2) study the hydrologic cycle in an American Monsoonal climate, (3) observe fluxes of water, water isotopes, solutes under American Monsoonal climate, and (4) assess the impact of these processes on paleoclimatic interpretations of soil-chemical profiles and soil-development processes.

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TITLE: Water Chemistry of Sediment Surface Coatings

PROJECT NUMBER: CR 76–199

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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 spectroscopy, 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: Three-dimensional fluorescence spectra were taken of both solid and dissolved materials in natural systems. It was found that the concentration of materials present in hydrologic systems could be calibrated against standards and the limit of the amount present could be stipulated. In cases where no other interfering fluorospheres were present, it was possible to obtain quantitative results and to specify the concentrations of the materials in water and on suspended sediment surfaces. Toxic materials of anthropogenic origin are usually found in the higher energy part of the fluorescence spectrum, about 220—320 nanometers. There is a natural separation of anthropogenic materials from natural materials as the latter tend to fluoresce in the visible part of the spectrum, usually in the wavelength region from 350—550 nanometers. Introduction of Rhodamine B as an internal standard allows quantitative comparison between samples. Several earth materials were measured using these techniques and the occurrence of cresols, para phenols and similar compounds were traced by EEM (Excitation-Emission-Matrix) fluorescence patterns as these materials were transported in the South Platte River from Chatfield Reservoir to Brighton, Colo. Studies performed on the Cedar River, Iowa, with an initial seepage run sampling of 17 tributaries and the mainstem in 1990, and continued with a similar sampling in 1991, showed that in natural sunlight the half-life of photolytic degradation for atrazine was between 38 and 318 hours in samples collected in 1990, and between 26 and 175 hours for samples taken in 1991. The amount of degradation that occurs in the tributaries has a direct correlation to the nitrate ion concentration in the tributary. A mathematical model was developed which allows prediction of the atrazine half-life in a surface water based on the nitrate concentration. It is:

$$\text{Atrazine photolytic half-life in hours} = 10^{(-\log(\text{nitrate concentration})/8361)/2.01))}$$

Calculated values agreed within 20 percent with measured values. Calculations were applied to each tributary to the Cedar River from Cedar Rapids, Iowa to Conesville, Iowa. The percent of photolytic degradation of atrazine during transport in the tributaries to this system ranged from 54 percent to less than two percent. Six tributaries had greater than 12 percent loss during transport and two tributaries exceeded 50 percent loss during transport.

Atrazine degrades by loss of side chain moieties to form the two, four, -dihydroxy-six-chloro-one, three, five, triazine as well as the dechlorinated molecule which is cyanuric acid. Preliminary studies using both Raman spectroscopy and Liquid Chromatography indicate the measurement of cyanuric acid in environmental systems can be done with detection limits of 2 x 10^{-8} mol/L (moles per liter). Preliminary data revealed relatively large concentrations of cyanuric acid in the Cedar River and its tributaries, in the range of 10^{-7} mol/L. Similar measurement in the Platte River found residue levels at about 10^{-8} mol/L level.

Examination of reverse osmosis membranes to detect characteristics of aging of the membranes was done using Raman Spectroscopy and Fourier Transform Infared Spectroscopy. These techniques view the vibrational band energies of the membranes. The Raman spectra were more definitive, and exhibited 20 major vibrational bands. Critical interpretations of these spectra were performed. These bands were assigned as acetate, hydroxyl, methyl and carbonyl functional groups. Bands at 1300, 1620, 1736 cm^{-1} (wave numbers) were found in aged membranes but not in new membranes. These spectra can be used to determine molecular changes that occur in these osmotic membranes as a function of time of service of the membrane. Surface enhanced spectroscopy (SERS) was employed to measure cyanuric acid in natural waters. Preliminary data indicate a detection limit at 1×10^{-9} molar in waters that are free of fluorescing materials.

Four proposals were written to other federal agencies and to programs within the agency. Two presentations were made, one to the U.S. Bureau of Reclamation and the other to the U.S. Department of the Army to present two of the proposals. Seven technical presentations were made. Two technical symposia, one national, one international, were organized and chaired. Technical consultation was given to the country of Yugoslavia, at their request, concerning waterborne transport of etiologic agents, their detection and identification.

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SURFACE-WATER CHEMISTRY

TITLE: Arid Regions Climate and Chemistry

PROJECT NUMBER: CR 82—207

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PROBLEM: Few guidelines have been established for the quantitative characterization of past climates in terms of proxy-climate data obtained in 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 light stable isotopes to an understanding of the timing an magnitude of past changes in the Great Basin terrestrial hydrologic cycle is in its infancy.

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

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

PROGRESS: North shore Pyramid Lake core (75 m) was subsampled at 10-cm intervals. Samples are being analyzed by the University of Michigan isotope facility. Truckee River/Pyramid Lake surface-water system continues to be monitored for change in ^{18}O and ^{13}C on a weekly basis. ^{18}O and ^{13}C profiles are being taken at one site on Pyramid Lake every month together with temperature and conductivity. Closed-basin lake stable-isotope model has been coupled to lake-thermal evaporation model and initial simulations of ^{18}O variation in the waters of Pyramid Lake are complete. Barotropic air-parcel trajectory analysis of 135 precipitation events occurring at the Tahoe Meadows site are complete. A weather/radiometer station has been installed at Sutcliffe, Nevada. Hostetler's thermal/evaporation model of Pyramid Lake was applied in a sensitivity analysis of lake-level change. The results of the simulations indicated that Lake Lahontan surface area increased by a factor of 5 as a result of the occurrence of a perpetual jetstream climatology. Initial mesocale modeling results performed in cooperation with NCAR indicate that Lake Lahontan and Lake Bonneville probably reached their maximum surface area partially as the result of lake-atmosphere feedback (lake-effect) processes. Recent radiocarbon age dates of the basal layer of rock varnish dates that coats an erosional terrace on Anaho Island indicate that Lake Lahontan achieved about half its maximum surface area between 12,000 and 10,000 years ago. It was during this time period that the first wave of Asians crossed the Bering Straits and occupied caves in Winnemucca Lake subbasin. Shallow-water seismic profiles of Pyramid Lake were run in September.

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TITLE: Research in Analytical Environmental Trace Element Chemistry and Its Impact on Water Quality

PROJECT NUMBER: CR 83–282

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

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

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

PROGRESS: (1) Development of technology was continued for the direct measurement of ultra-trace (nanogram/liter) concentrations of constituents in hydrologic systems by inductively-coupled plasma mass spectrometry. Techniques and methodology were pioneered for the measurement of stable isotope ratios of selected heavy metals at trace (microgram/liter) concentration levels in natural waters. Techniques for absolute quantitation by stable isotope dilution analyses were developed. Instrumentation modifications were investigated to improve measurement precision, stability and sensitivity. (2) Research was completed to develop a new technique for measuring the isotope ratio of potassium at trace concentration levels. A flame ionization-mass spectrometric techniques utilizing an air/acetylene premixed flame was developed. The technique is being used in groundwater studies at the Cape Cod (Mass.)

Hazardous Waste Site as a geochemical tracer. (3) 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 be collected and concentrated trace metals was evaluated and found to be suitable for field studies. (4) Research was initiated to use sedimentation field fractionation coupled with ICP/MS to study the distribution of trace elements in various size fractions of colloidal material. (5) Research was performed, including field trips, to measure the occurrence, distribution and fate of trace metals in the Mississippi River system. This includes the investigation of interaction of trace metals with other water chemical parameters, with emphasis on the distribution between various size fraction of suspended material, silts, calloids, etc.). Studies were performed to representatively collect and separate statistically valid and uncontaminated samples. Field studies were also carried out to determine interactions of contaminants with each other and suspended sediment at primary mixing zones below confluences of tributaries. (6) Research was performed to measure the relationship between water chemistry constituents and the occurrence and distribution of benthic invertebrates populations in rivers and streams. Field work was performed in the Gibbon and Firehole Rivers in Yellowstone National Park and rivers and streams in the Catskill Mountains, N.Y. (7) Studies are underway to evaluate the chemical composition of ice layers in glaciers from the Wind River Mountain range in Wyoming. These studies will assist in evaluating climatic changes in atmospheric depositions. (8) Research was initiated to study the water quality of the Colorado River system and the impacts from Glen Canyon dam operation on the ecology and water quality of the river systems.

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

PROJECT NUMBER: CR 83—284

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

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

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

PROGRESS: A summary of acid rain and atmospheric pollutant damage to carbonate stone was published in Conservation of Monuments in the Mediterranean Basin, Proceedings of the 1st International Symposium, held in Bari, Italy. This report supports, with previously unpublished data, the conclusion that dissolution in uncontaminated rain accounts for about two-thirds of observed calcium carbonate dissolution for marble and limestone. Acids in rain and sulfur oxides in air appear to cause the remaining calcite dissolution. Several sections in "Acidic Deposition: State of Science and Technology, Report 19, Effects of Acidic Deposition on Materials," National Acid Precipitation Assessment Program (NAPAP), have been authored (or coauthored) by project staff. Sections in Report 19 contributed by this project include discussion of runoff experiments, and results (coauthored with P.A. Baedecker of the Geological Division), examination of stone wetness and water transport (coauthored with V.G. Mossotti of the Geological Division) and a summary of carbonate stone erosion and surface recession (coauthored with P.A. Baedecker of the Geological Division and others). These results demonstrated quantitatively the effect of dry deposition of SO_2 gas on the chemical erosion of the carbonate stone surface by determining anion concentrations in runoff solution.

Significantly, in assessing acid rain economic impacts, wet deposition of free acidity was not the dominant cause of calcium carbonate dissolution of the stone specimens at the most acid rain impacted exposure site. Investigations of the physical processes involved in stone wetting were presented also in Report 19. Diurnal moisture cycles (that is, formation of condensation on the stone surface) and direct rainfall are the two primary sources of moisture affecting the stone surface. Each of these sources can influence the deposition of SO_2 to the carbonate stone surface and thus increase carbonate stone damage.

A paper reporting the molecular weight and aggregation tendency of a reference soil fulvic acid has been published in the journal Analytical Chimica Acta. The study found that the number average molecular weight of Armadale Horizon Bh fulvic acid increases from 733 to 977 daltons above 7mg/ml; this behavior is attributed to molecular interactions at high fulvic acid concentrations. A manuscript describing electrostatic and functional group heterogeneity effects on the acid dissociation reactions of Suwannee River fulvic acid has been published in the Journal of Environmental Science and Technology. This paper demonstrates that electrostatic effects are successfully accounted for using the Debye-Huckel theory. Titration data can be well-fitted with three intrinsic acid dissociation constants (each applying to one-third of the carboxylate binding sites) of pKint 2.53 (+0.16), 3.75 (—0.04) and 5.65 (+ 0.05). A manuscript presenting structural studies of Suwannee River fulvic acid, which demonstrates quantitatively the significance of a substituted malonic acid functional groups, received Director's approval for publication. A report describing the dissolved solutes budget of a small alpine basin in Colorado, has been published in the International Mountain Watershed Symposium—Subalpine Processes and Water Quality, edited by I.G. Poppoff, C.R. Goldman, S.L. Loeb, and L.B. Leopold. This study offers support to the recent hypothesis of extensive chemical denudation in mountainous areas, especially those which contribute large volumes of water to stream flow.

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TITLE: Comprehensive Organic Analysis of Water

PROJECT NUMBER: CR 84—285

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

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

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

SURFACE-WATER CHEMISTRY

PROGRESS: Fiscal year 1991 was used to complete and summarize various research projects and begin a new research project. Larry Barber and Jennifer Field both completed their Ph.D. studies at the Cape Cod Toxic Waste research site in Massachusetts. Larry's thesis topic addressed effects of aquifer particle size and mineralogy on sorption and transport of nonionic organic contaminants in ground water. Jennifer Field's thesis addressed the fate and transformations of surfactants in sewage-contaminated ground water. Several journal articles and meeting presentations were derived from these two thesis projects.

The project chief summarized a decade of data on the characterization of natural organic substances in water by writing a book chapter on "Organic substance structures that facilitate contaminant transport and transformations in aquatic sediment" and a book chapter on "Chemistry of dissolved organic matter in rivers, lakes, and reservoirs". A major finding of these summary reports is that the chemistry of dissolved organic matter is not infinitely complex, but that the decay process that produces organic matter converges to certain molecular structures, such as substituted malonic acids, aliphatic alicyclic rings, and so forth, can be used to explain much of the structure and chemistry at the molecular level.

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SURFACE-WATER CHEMISTRY

TITLE: Solid Phase Chemistry and Related Environmental Processes

PROJECT NUMBER: CR 89–316

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

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

PROGRESS: This project was started in FY89. In FY90, office and laboratory facilities were obtained and stocked with operational supplies. In FY 91, surplus analytical instrumentation (graphite furnace/Zeeman and flame atomic obsorption spectrometers, inductively-coupled plasma and direct-current plasma spectrometers, 3.4 m optical emission spectrograph, gas chromatograph) were obtained. Field experience was gained on Mississippi and Colorado Rivers water quality studies. Trace element studies of suspended sediments and alpine lake waters were initiated. Collaboration with the Colorado District program at the Rocky Mountain Arsenal was initiated with a study of induced contaminant-transport within a confined aquifer.

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

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

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

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

PROGRESS: A manuscript entitled "Geochemical Fluxes of Arsenic, Iron, Manganese, and Phosphorus in Lake Oahe, South Dakota" has been approved for publication as Chapter G of a U.S. Geological Survey Water-Supply Paper, "Origin, Transport, and Fate of Arsenic-Contaminated Sediments in the Cheyenne River System, South Dakota." A comparison between diffusive fluxes out of the sediment column and accumulation rates within the uppermost part of the sediment column indicate that rapidly accumulating sediments near the Cheyenne River Delta concentrate solid-phase As, Fe, Mn and that sediments deposited farther from the delta diagenetically recycle much of the As and Mn that reaches the sediment surface. A paper entitled "Environmental Reconstruction of a sediment Core from Lake Oahe, South

Dakota" was presented at the Fall 1990 Meeting of the American Geophysical Union. Radiometric dating models allowing for time-dependent sediment accumulation reveal an exponentially decreasing rate since creation of the reservoir in 1959. Superimposed on the long-term trend of decreasing sedimentation are fluctuations reflecting monthly variations in suspended solids loadings. Detailed distributions of more than 15 elements record significant hydrologic events within the sub-basins of the Cheyenne River Basin. Periods of high river flow are associated with high Ca content originating primarily from input of Oligocene White River sediments in the distant South Dakota Badlands. Predominating during periods of low flow are locally originating trace elements (Ba, Cr, V, Zn) and associated organic matter derived from erosion of steep shoreline bluffs consisting of Cretaceous Pierre Shale. High sedimentary As content correlates with solids loading from the Belle Fourche River which received As-rich mine tailings until 1975. A paper entitled "Transition Metal Chemistry of the Upper Arkansas River, Colorado" was presented at the Monterey, California Technical Meeting on Toxic Substances Hydrology and will be published in the proceedings from that meeting. During low flow, the concentration of dissolved iron appears to be controlled by equilibrium with amorphorus-iron phases, and the manganese and zinc partitions to the particulate fraction in the downstream direction. Under high-flow conditions, the distribution patterns of all three metals are controlled by physical factors, such as discharge and turbulence. The downstream attenuation of sedimentary iron, manganese, and zinc follow different patterns. Iron is added to the river sediments by acid-mine drainage near Leadville and there is no increase or sustained partitioning of iron to the sediment downstream. Manganese and zinc also are contributed by contaminant inflows near Leadville but appear to be reacting between the water column and bed sediment in a downstream direction. A substantial fraction of these sedimentary metals is present as an easily extractable phase. Iron occurs mostly in the mineral fraction of the bed sediment. Research continues on the sedimentary geochemistry of Lake Baikal, Southeastern Siberia, USSR. A paper entitled "Geochemical and Mineralogic Indicators of Sedimentation in Lake Baikal, Southeastern Siberia, USSR" was presented at the 1991 Spring Meeting of the American Geophysical Union. Cores from sites 307 (Academician Ridge) and 309 (hydrothermal vents) exhibited a reddish-brown surficial oxidized layer and one or two additional oxidized layers at depth. These oxidized layers are not uniformly distributed within surficial sediments of Lake Baikal. The oxidized sediments are enriched in Fe and Mn relative to adjacent reduced sediments. These oxidized zones apparently represent time intervals when sedimentation was much slower than intervals represented by underlying reduced sediment. Thus, the process of diagenetic remobilization, upward migration, and oxidation of Fe and Mn near the sediment-water interface has ample time to develop a relatively thick (up to 13 cm) oxidized layer. Mineralogic evidence for substantial variation in sedimentation rates is given by the presence of altered golden-brown biotite and Fe-rich integrated smectite in oxidized layers versus unaltered black biotite and Fe-deficient smectite in adjacent sediments. Oxidized sediment layers were in contact with oxygenated bottom waters for long periods of time (10's to 100's of years)—a situation that would encourage the subaqueous weathering of biotite mica and the rearrangement of detrital smectite to an intergrade phase.

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

PROJECT NUMBER: NR 78—092

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

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

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

PROGRESS: Based upon selective extraction studies (Landa, E.R., 1982, Leaching of radionuclides from uranium ore and mill tailings: Uranium, v. 1, p. 53—64), we identified alkaline earth sulfate minerals and hydrous ferric oxides as potential hosts for Ra-226 in uranium mill tailings (UMT). Subsequently we demonstrated the enhanced leaching of radium from UMT by the action of sulfate reducing bacteria (Landa, E.R., Miller, C.L., and Updegraff, D.M., 1986, Leaching of Ra-226 from uranium mill tailings by sulfate-reducing bacteria: Health Physics, v. 51, p. 509—518).

In our recent investigations UMT were anaerobically incubated in the presence of H_2 with *Alteromonas putrefaciens*, a bacterium known to couple the oxidation of hydrogen and organic compounds to the reduction of Fe(III) oxides. There was a direct correlation between the extent of Fe(III) reduction and the accumulation of dissolved Ra-226. In sterile tailings in which Fe(III) was not reduced, there was negligible leaching of Ra-226. The behavior of barium was similar to that of radium in inoculated and sterile systems. These results demonstrate that under anaerobic conditions, microbial reduction of Fe(III) may result in the release of dissolved Ra-226 from UMT. The role of *A. putrefaciens* and another iron-reducing microorganisms (GS-15) in the reduction of uranium was demonstrated in studies done in cooperation with project NR—136. The project chief participated (for the World Meteorological Organization) in an International Atomic Energy Agency (IAEA) coordinated project to assess the radiological consequences in the Soviet Union of the Chernobyl accident. Water and sediment samples were collected in the vicinity of the Chernobyl reactor during the summer of 1990. The results will be published as an IAEA proceedings volume.

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TITLE: Carbon Fluxes in Hydrologic and Geologic Processes

PROJECT NUMBER: NR 79—099

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PROBLEM: Carbon fluxes are an important aspect of many hydrologic and geologic processes. For example, on a global scale, rising atmospheric 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 14C 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-milliliter 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.

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SURFACE-WATER CHEMISTRY

TITLE:	Geochemical Cycling of Trace Elements and Nutrients in Natural Water Systems
PROJECT NUMBER:	NR 81–109
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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 watersheds are being continued. A study applying a geology-based method for predicting stream sensitivity to acidification by acid rain to streams in the Atlantic Coastal Plain Physiographic Province has been completed.

The method works well in undisturbed watersheds, but natural controls on water chemistry are masked in watersheds heavily disturbed by man. Investigation of the factors controlling the major ion chemistry of streams in the Blue Ridge and Valley and Ridge Physiographic Provinces of Virginia and Maryland has identified bedrock geology as the primary controlling factor. Studies of the time and pH dependent leaching of ions from deciduous and coniferous foliage and of the spatial variability and collector requirements for sampling throughfall volume and chemistry under a mixed-hardwood canopy have been published. Research on chemical weathering in an alpine watershed developed on granite bedrock has disclosed that weathering of intergranular calcite plays a major role in determining stream water chemistry at that site. Investigations of changes in stream chemistry during episodic events in mid-Atlantic watershed systems are continuing. Chemical changes are related to shifts in the proportions of water reaching the stream from watershed contributing areas which vary with antecedent moisture conditions and storm intensity and duration. The first stage of laboratory studies on the kinetics of biotite and chlorite dissolution have been completed. Field and laboratory studies of whole rock weathering of the Catoctin Greenstone are in progress. These studies in conjunction with watershed investigations, are elucidating the effects of bedrock type on natural water compositions.

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TITLE: Distribution and Speciation of Metals in Sedimentary Environments

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

SURFACE-WATER CHEMISTRY

PROGRESS: After completion of a cooperative study with personnel from EPA to evaluate toxicity tests of sediments from the Calcasieu River Estuary (La.), further study of the bottom material and suspended matter has been made. Preliminary analyses showed that, although the bottom sediments had large concentrations of metals, the water column and suspended sediment that was separated by tangential flow filtration of the water column did not. Because the origin of metals to the bottom sediments did not appear to be either the water in the water column or the suspended material separated by tangential flow filtration from the water column, it was hypothesized that material which had not heretofore been collected or analyzed must play a major role in the transport of heavy metals in the Calcasieu Rivery Estuary. The aggregated suspended material that appears in the water column had never been collected or analyzed. This material which consist of suspended organic and inorganic matter was collected in 0.5 nm drift nets. Analysis of this material showed that the total metal concentrations in the drift were much larger than the total metal concentrations in the sediment. Total concentrations of metals are not sufficient to determine the impact of the metals on the environment and it is important to determine the speciation of metals with respect to the organic component of the samples. Mercury is known to be 10 to 100 times more toxic when organically-complexed that when in the inorganic state. To determine if the metals were associated with the organic matter, the drift and bottom sediments were extracted using supercritical carbon dioxide which, if used without modifiers, will extract only nonpolar organic compounds. Extractions using pressures of 100 to 400 atmospheres were done to fractionate the organic matter. The fractions were analyzed to determine which ones contained metals of interest. These fractions contained 10 to 30 percent of the total mercury that was extracted from the drift and sediment samples; the organic compounds in these fractions included carotenes, fatty acids and nonpolar synthetic chemicals. Addition of methanol to supercritical fluid carbon dioxide is used to extract polar organic compounds. The remaining mercury in the drift and more than half of the mercury in the sediment samples were extracted using supercritical fluid carbon dioxide modified with methanol. Methanol modified supercritical carbon dioxide extracted chlorophyll and chlorophyll degradation products. The largest amounts of mercury and copper were extracted with pigments which suggests that these metals are associated with the algal component of the drift and bed sediments. These results indicate that algae in the drift of the Calcasieu River is transporting heavy metals. This same metal polluted material is part of the food chain. Analytes extracted by supercritical fluid extraction are collected in small volumes of organic solvents. Because these samples are composed of organic compounds in organic solvents they are not suitable for analysis using the conventional atomic absorption techniques. Because the customary cold vapor method for mercury determination requires that organic compounds in the sample be eliminated, we have had to develop a method for analysis for mercury using a graphite furnace and atomic absorption spectroscopy utilizing palladium as a sample modifier

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

PROJECT NUMBER: WR 57—076

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

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

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

PROGRESS: During the 1991 fiscal year a final interpretive report was completed based on the results of coprecipitation experiments in which cadmium was present in various proportions during oxidation of divalent Mn by aeration of aqueous solutions at pH 8.0, 8.5, and 9.0. The increased yield of Mn^{4+} oxide observed in these experiments was explained on the basis of coordination chemistry and reaction kinetics. A postulated unstable intermediate having the structure of hausmannite with Cd^{2+} replacing Mn^{2+} is believed to explain the kinetically favored reaction path leading to Mn^{4+} containing oxides such as $Cd_2Mn_3O_8$ and Mn_5O_8 produced during titrations and subsequent aging.

Additional experimental results on aluminum hydrolysis reaction rates and product species indicate that there is apparently a change in chemical reaction mechanism and form of product above pH approximately 5.4, and with increased rates of Al and OH addition. Application of nuclear magnetic resonance (NMR) analysis to the speciation was begun under an informal joint arrangement with Kevin Thorn of the Organic Polyelectrolytes project, Denver. Combining the results with those obtained by the ferron procedure for polymer species determination should lead to major improvement in understanding the $Al(OH)_x$ polymerization process.

Study of historical data for major anion concentrations and loads demonstrate upward trends for sulfate and chloride for all or parts of the period from 1905 to 1990 on some major U.S. streams, including the St. Lawrence and lower Mississippi, but other streams, notably Columbia River at The Dalles, Oreg., show very little change. A few streams strongly affected by industrial pollution and mine drainage during the 1940's and 1950's showed substantial improvement in low-flow quality during the 1970's and 1980's. Hydrogeochemical properties of stream basins that may control their sensitivity toward water-composition changes and anthropogenic factors such as reservoir construction and flow regulation can help explain these trends and may suggest new topics for hydrologic research. These subjects will be discussed in a chapter in preparation for a forthcoming volume in the National Water Summary series.

Mineralogic work on manganese oxides and related precipitates from Pinal Creek, Arizona, affected by mine-waste show that the material includes some carbonate species, one of which is the calcium manganese carbonate, kutnahorite. This material also was synthesized in a laboratory experiment in which ground water from the vicinity of the streambed precipitate collection site was raised in pH and aerated.

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

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

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

PROGRESS: Studies of the distributions and fate of anthropogenic organic compounds in Susuin Bay started in January 1991. Samples of water, suspended and bed sediments, and the asiatic clam *Potamocorbula amurensis* were collected and analyzed. The dissolved phase contained trace levels of 2-nitrophenol, the herbicides diuron, simazine and atrazine, and a flame retardant tris-2-chloroethylphosphate. Suspended sediments were collected from two sites using a continuous flow cartrifuge. In addition to diuron and 2-nitrophenol, these samples contained a large suite of aliphatic and polynuclear aromatic hydrocarbons. Bed sediments also contained the same suites of hydrocarbons. Methodology was developed for the determination of these compounds in the Asiatic clam. It was determined that tidal fluxes had a significant effect on the distributions of hydrocarbons derived from terrestrial and anthropogenic sources. The asiatic clam was a good bio-indicator of these hydrocarbons. *Potamocorbula amurensis* bioaccumulated alkanes, stearanes and hopanes (molecular markers) as well as polynuclear aromatic hydrocarbons. Bioconcentration of these compounds in *Potamocorbula amurensis* is being reported for the first time.

SURFACE-WATER CHEMISTRY

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Page 251 follows

SURFACE-WATER HYDROLOGY

TITLE: Precipitation-Runoff Modeling of Watershed System

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

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

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

PROGRESS: Completed first phase of the development of the Modular Hydrologic Modeling System (MHMS). The X-windows based MHMS was implemented on a SUN and a Data General workstation. The modular library currently includes modules from the daily version of PRMS and selected modules from the National Weather Service NWSRFS model and the Corps of Engineers SSARR model. Modeling of flow processes at the H. J. Andrews Experimental Watershed was begun as a joint effort with U.S. Forest Service research personnel. Development of an orographic precipitation model for the Gunnison River basin continued. Exploratory work on the relations among weather types, precipitation, and topography continues. A joint project with National Oceanic and Atmospheric Administration (NOAA)

Forecast Systems Laboratory and Denver Urban Drainage and Flood Control District was initiated to investigate the applications of NEXRAD radar precipitation data to hydrologic modeling. Detected subglacial conduits using ice radar and provided experimental evidence for conduit expansion and contraction. Investigation of bias and uncertainty in estimates of model-error variance of regional regression relations developed using weighted least-squares was continued. A Monte Carlo sampling and regression simulation technique was developed and coupled with observed data analyses to investigate the adequacy of a quantile variance equation and to quantify the uncertainty in estimates of model-error variance using an iterative weighted least-squares procedure.

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SURFACE-WATER HYDROLOGY

TITLE: Statistical Analysis of Errors in Hydrologic Models

PROJECT NUMBER: CR 83—279

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

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

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

PROGRESS: (1) Investigations of properties of the random topology channel network model, especially for large networks [our strategy in looking at the effect of model input error has been to randomize various components of model input, including channel segment properties, such as length, and channel segment configuration. This has been done primarily via the random topology model used by geomorphologists since the 60's. Hence, our investigations into model input error have led to a number of related studies on the properties of this and other random network models]: (a) Derived distribution of area drained as a function of distance along the mainstream; (b) Derived properties of the width function of a channel network, including the mean and variance of the width as a function of distance from the outlet, and the distribution of the peak width [the width function is the network i.u.h., using translation channel routing]. (2) Investigations of spatial random network models [the random topology model does not give a unique spatial definition to networks being modeled. Hence, we have seen the need to look at random models that are well-defined spatially; we have used rectangular grids to do this]: (a) Studied application of the one-parameter Gibbsian family of distributions (well-known for applications in thermodynamics and statistical mechanics) for modeling spatial behavior of channel networks; the parameter is a measure of drainage efficiency of the network: (i) Developed Markov chain procedure for simulating networks under the Gibbsian distribution; (ii) Developed parameter estimation procedures for networks defined using digital elevation data (i.e., for "topographic trees"); (iii) Developed regionalization methods for predicting the Gibbsian parameter as a function of map scale; (iv) Looked at methods for using this model to predict network width function; (v) Applied methods developed using digital elevation data for Willow Creek, Mont.: (b) Investigated fractal properties of spatial models as measured by the behavior as the grid spacing grows smaller. (3) General extensions of previous results giving hydrologic response as a function of fundamental basin characteristics: (a) Previous results (i.e., i.u.h. peak as a function of network magnitude) have assumed linear channel routing with a constant basin-wide velocity and no overland flow delay. Some time has been spent looking at how such results might be generalized (nonlinear routing, spatially variable velocity, etc.); (b) Investigated optimal ways to estimate hydraulic parameters such as the effective basin-wide velocity. (4) Work with Bob Lichty on error analysis of regionalized flood magnitudes: (a) Investigated influence of climatic factors on regionalization error; (b) Mapped flood distribution moments based on ensemble averaging. (5) Statistical analysis of hydrologic data: (a) Developed new methods for model identification analysis for periodic autoregressive moving average time-series models [these models are extremely useful for characterizing stochastic properties of seasonal time-series such as monthly streamflows]; (b) Developed a new efficient method of prediction for spatial regression models with correlated errors using maximum likelihood methods. The methods can be used for evaluating uncertainty in spatially distributed inputs to hydrologic models; (c) As part of the global change research initiative, developed a stochastic model for generation of joint-station monthly streamflows on the Upper Gunnison River Basin. The model will be used for studies on the sensitivity of the Gunnison River Basin to climatic change.

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TITLE: Transport and Degradation of Organic Substances in Streams

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

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

PROGRESS: The trihalomethane formation potential of water from the Kentucky River ranged from 59.7 to 731 and averaged 240 micrograms per liter for 153 determinations at 25 degrees Celsius. Multiple-linear regression analysis of the data indicated that pH was the most significant variable in determining the formation potential, followed by the dissolved organic carbon concentration. The initial free chlorine concentration had only a slight effect. The total trihalomethane formation potential was not dependent on the bromide concentration. The formation of the brominated trihalomethanes, however, was strongly dependent on the bromide concentration, with only trace levels of bromide producing significant concentrations. Trends in the seasonal transport of halogenated organics sorbed on the suspended sediment of the Lower Mississippi River were related to periods of pesticide and herbicide applications in the midwestern United States. Large increases in the hexachlorobenzene concentration were attributed to industrial input from the Ohio River. Large increases in the hexachlorobenzene concentration were also observed in the industrial corridor of Louisiana. High concentrations of polychlorinated biphenyls (PCB's) were introduced by the Ohio River and persisted downstream in the Mississippi River. Differences in the ratio of the concentrations of chlordane and nonachlor may allow determination of whether these compounds resulted from resuspension of bottom sediments or from surface runoff.

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SURFACE-WATER HYDROLOGY

TITLE: Paleohydrology and Climate Change

PROJECT NUMBER: CR 90-321

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

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

APPROACH: Interdisciplinary, process-oriented research will be used to study past and present hydrologic and climatic conditions. The research includes: (1) The paleohydrologic research will consist of selecting several basins in different climatic regions to construct the paleofluvial history of each river basin. Using different methods (such as step-backwater, critical depth, and tractive force), estimate paleodischarges. Using a variety of geochronologic techniques (dendrochronology, carbon 14, thermoluminescence, and other absolute- and relative-age dating techniques), improve methods to make high-resolution time sequences of alluvial stratigraphy; (2) Conduct instream, laboratory and numerical modeling studies to improve paleohydrologic methods of estimating velocity and discharge, and; (3) Analyze hydrologic, paleohydrologic, and climatic data to quantify long-term variability and to improve the understanding of the links between climate, fluvial processes, and hydrology.

PROGRESS: The study and report on the paleoflood hydrology of Arthurs Rock Gulch, Colorado Front Range are essentially finished. The study investigates the paleofluvial history of the river basin, and the development and testing of methods used in paleofluvial studies in mountain rivers. Additional paleohydrologic sites in the Rocky Mountains have been identified for research.

Collected high-flow data at the North Saint Vrain Creek for river hydraulic studies at the Rocky Mountain Hydrologic Research Center (the Rocky Mountain Hydraulic Laboratory) in Allens Park, Colo., to improve methods to estimate velocity, and discharge, and paleodischarge in mountain rivers.

REPORTS PUBLISHED 1990-1991

Jarrett, R.D., 1990, Hydrologic and Hydraulic Research in Mountain Rivers: Water Resources Bulletin, v. 26, no. 3, p. 419—429.

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

PROJECT NUMBER: NR 69—019

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PROBLEM: Technical solutions to the problem of investigating and managing waste movement and disposal in regulated rivers, estuaries, and embayments require qualitative and quantitative 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: Project efforts have been directed to the following research areas during the past year: (1) Conducted investigation of the seasonal tidal mass exchange between a submersed aquatic-vegetation (SAV) bed and the adjacent channels of a tidal river. Initial analyses of field-measured results indicates that the basic hypothesis of approximately radial ebb- and flood-flow from and into the bed with changing tide is fundamentally correct--even though simplistic. Partial results of these studies are being presented at an international society conference in mid-July, 1991, and are reported in the societal journal. This study is being conducted jointly with the Wetland Studies Project. (2) Completed analysis and processing of National Mapping Division digital line graph (DLG) data to generate grids and subgrids for two-dimensional, dynamic modeling of a riverine floodplane. This investigating demonstrates the feasibility of using DLG data to derive two- and three-dimensional grids for flow/transport models. However, it also revealed that additional point data must be included for relatively flat terrain shown on topographic maps and included in the DLG files in order to make this approach to model development less costly and less time consuming. (3) Initiated work on the implementation and calibration of a hybrid version of the ECOM—3D—SI model for Boston Harbor and Massachusetts Bay. Enhancements and changes are being incorporated to effect and verify the transfer of this numerical code to workstations and x-terminals. The feasibility of organizing and simplifying the data input/output for such models through the use of self-defining, network common data form (netCDF) filing is under investigation. This project is being conducted jointly with the Branch of Atlantic Marine Geology, Geologic Division. (4) Continued investigation into the physics and numerical methods for best treatment of the nonhomogeneous terms--bed slope, frictional (turbulence and drag) slope, nonprismatic geometry, lateral flow, and wind (shear and surface drag) stress--for the fully dynamic, open-channel flow equations. This effort translated directly into some improvements in one-dimensional modeling capability. (5) Analyzed data and developed operational two-dimensional flow/ transport model of the tidal Pamlico River, N.C. Analyzed data—up to the final steps of developing a model-for the tidal Neuse River, N.C. The Pamlico River model and the almost-completed Neuse River model, together with field measured flow data, were turned over to another NRP project for model calibration, enhancement, and operational use. (6) Continued examination of the numerical convergence properties of a two-dimensional, vertically integrated, hydrodynamic/transport model based upon the alternation direction implicit (ADI) technique when used with prototype data from an estuarine regimen having appreciable flooding and dewatering of tidal flats adjacent to narrow channels. Experimental numerical results underscore the space/time (wave dependent) restrictions found necessary to insure proper wave propagation and convergence. This physics-based constraint applies to all models. Partial results have been presented at a national society meeting and are pending publication in a widely circulated society journal. (7) The continued study of the flooding and dewatering of shallow regions in a numerical simulation model has resulted in an improved means for treating the hydrodynamics of this phenomena, but one in which successful function of the coupled transport equations is not possible. A means is being sought whereby the improved stability of hydrodynamic treatment will not invalidate the numerical treatment of the transport equations. (8) Continued to provide consultation and—in several cases—direct assistance to many District Offices, either conducting or planning to conduct cooperatively funded numerical simulation studies of both riverine and estuarine flow and transport.

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Baltzer, R.A., Regan, R.S., and Schaffranek, R.W., 1989, Time-dependent data system, Overview: U.S. Geological Survey Open-file report 89—0631, 5 p.

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TITLE: Computational Hydraulics for Surface Water Problems

PROJECT NUMBER: NR 79-096

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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: Project chief has been on leave of absence to teach in Taiwan.

SURFACE-WATER HYDROLOGY

REPORTS PUBLISHED 1986—1991:

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-----1989, A numerical scale model for simulating unsteady alluvial-channel flow: Technical Report prepared for Sedimentation Committee, Interagency Advisory Committee on Water Data, 72 p.

-----1990, Computational open-channel hydraulics for movable-bed problems: 1990 National Hydraulic Engineering Conference, ASCE, July 30—August 3, 1990, San Diego State University San Diego, Calif., Proceedings.

-----in press, Modeling unsteady alluvial-channel flows by the multimode characteristic method——Theory and algorithm formulation: Journal of Engineering Mechanics, American Society of Civil Engineers, v. 116.

Lai, C., Schaffranek, R.W., and Baltzer, R.A., 1989, Frictional resistance treatment in unsteady open-channel flow simulation: International Conference on Channel Flow and Catchment Runoff, Centennial of Manning's Formula and Kuichling's Rational Fora, May 22—26, 1989, Charlottesville, Va., University of Virginia, [Proceedings], p. 688—698.

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

TITLE: Simulation Modeling of Hydrodynamic Systems

PROJECT NUMBER: NR 80—104

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

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

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

PROGRESS: Project efforts over the past year have concentrated in the following research areas: (1) Continued evaluation of varied methods and alternative simulation procedures for handling open-boundary conditions in numerical solution of the unsteady-flow equations; model sensitivity and simulation results are shown to be highly correlated to open-boundary condition specification and numerical treatment. Partial results of these studies have been published and presented at international society conferences. (2) Conducted performance tests of various technical and structural modifications to the branch-network unsteady-flow model in order to extend its use in workstation and microcomputer environments. Resultant modifications to the matrix solver routine, channel-geometry treatment, and overall code modularity have effected up to a 20-percent increase in simulation efficiency for complex open-channel networks. (3) Continued investigation into the physics and numerical treatment of the nonhomogeneous terms representing bed slope, frictional slope, nonprismatic geometry, lateral flow, and wind stress in the partial differential equations of unsteady open-channel flow. Improved and extended numerical treatment of channel geometry and frictional resistance in the branch-network unsteady-flow model based on findings. Partial study results have been published in international conference proceedings and prepared for book publication. (4) Conducted extensive simulation tests of a complex two-dimensional vertically-integrated hydrodynamic/transport model, based on the Alternating Direction Implicit (ADI) solution method, to effect and verify transporting the numerical code to workstation and extended-memory microcomputers. (5) The numerical convergence properties of a two-dimensional vertically-integrated ADI hydrodynamic/transport model have been examined and verified using prototype data from a complex estuarine system having a significant tidal amplitude and extensive tidal flats and wetlands. Numerical experiments with the ADI method confirm findings restricting the time and space discretization on the basis of topographic and bathymetric properties to insure proper wave propagation and numerical convergence. Through coupled solution of the transport equation, horizontal density forcing in the Potomac Estuary is being investigated under varied initial and open-boundary conditions. Partial results have been presented at national society conferences and published in the conference proceedings. (6) Provided consultation and(or) direct assistance to several District Offices conducting numerical modeling studies to investigate saltwater intrusion, determine water-quality conditions, and compute streamflows using models developed within the research project.

REPORTS PUBLISHED 1986—1991:

Lai, Chintu, and Schaffranek, R.W., 1986, Discussion of Computation of dynamic waves in channel networks: American Society of Civil Engineers, Journal of Hydraulic Engineering, v 112, no. 3, p. 246—249.

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Schaffranek, R.W., 1986, Hydrodynamic simulation of the upper Potomac Estuary: American Society of Civil Engineers, Water Forum '86: Conference on World Water Issues in Evolution, August 4—6, 1986, Long Beach, Calif., [Proceedings], p. 1572—1581.

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

PROJECT NUMBER: NR 82—125

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

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

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

PROGRESS: Progress was made in four areas of investigations. (1) The network design comparison study for the World Meteorological Organization was concluded and improvements in the Network Analysis Using Generalized Least Squares method reported. (2) Applicability of the Generalized Least Squares regression program used for regional regression studies was extended to include low flow regionalizations. This new low flow regression method will allow users to include many low-flow partial-record stations in a regional study in a sound statistical manner and may lead to improved estimates of low flow characteristics. (3) A method of estimating urban stormwater loads at unmonitored sites using regional regression methods was extended to include larger areas through an accumulation scheme. This may help cities comply to new U.S. Environmental Protection Agency urban stormwater load regulations. (4) A validation of the Delaware River model, developed to study hydrologic effects of climate change, was made by comparison to a daily model. The model was extended to include estimates of the position of the salt front in the Delaware estuary.

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Gilroy, E.J., and Tasker, G.D., 1990, Multicollinearity and influential observations in hydrologic model selection, in Berk, K., and Malone, L., ed., Computing science and statistics: 21st Symposium on the Interface, [Proceedings], p. 350—354.

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TITLE:	Regional Hydrologic Processes
PROJECT NUMBER:	NR 84—133
PROJECT CHIEF:	Landwehr, Jurate M.
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PROBLEM: The regional nature of hydrologic processes is generally defined in terms of shared meteorologic and basin characteristics. Inferences have been attempted by regressing the measures of hydrologic interest against such characteristics. Such treatment has been insufficient to fully explain the variations or extremes in discharge patterns observed within a geographic area. Long-term influences such as decadal to centennial climatic fluctuations need to be considered, and the stochastic structure of the hydrologic process itself needs to be better defined.

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

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

PROGRESS: The delineation of the Hydro-Climatic Data Network (HCDN) is nearing completion, after a year of extensive checking of the values in the WATSTORE Daily Values and Header and Basin Characteristics file. Work has been carried out in concert with at least one data expert in each state office to assure quality control. Header and identifying information for each of the 1600+ stations has been checked against the published records and a surprising number of discrepancies have been identified, as well as several major problems with the WATSTORE Data storage and retrieval system. A briefing on the content as well as status of the work was presented (in a poster paper) at the U.S. Geological Survey Global Change Research Forum in March, 1991.

Extensive time series analysis (in both the frequency and the time domain) has been carried out for the $\delta^{18}O$ and $\delta^{13}C$ time series found in DH—11, a calcitic core extracted from the wall of Devil's Hole in Nevada. The records present a challenge to the Milankovitch theory of climate change, the currently most accepted explanation of the timing of the ice-ages. At the request of the conveners of a special symposium on climate variation during the annual GSA meetings, the work to date was summarized in a series of talks. Several papers are in preparation.

A paper, prepared jointly with Tim Cohn and Ken Potter (University of Wisconsin) on "Common Concerns Related to Paleoflood Frequency Analysis." The paper is in review as a chapter in a U.S. Geological Survey Water-Resources Investigation Report (edited by Will Thomas and Cliff Hupp) which will serve as a technical manual on the use of paleo-methods in flood frequency analysis.

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

PROJECT NUMBER: NR 88—143

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PROBLEM: A stable moving platform is needed to accommodate scientists so that large volumes of complex and continuous data can be carefully and rapidly collected and precisely measured and analyzed immediately after collection.

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

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

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

TITLE: Continental Hydrology and Global Climate

PROJECT NUMBER: NR 88–144

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

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

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

PROGRESS: (1) A detailed study was undertaken to assess the meaningfulness of potential evaporation rates and values of soil moisture produced by climate models. It was demonstrated that climate models greatly overestimate the value of potential evaporation, relative to conventional definitions, and that modeled soil moisture is seriously underestimated in seasons of water shortage. The cause of these errors has been identified, explained, and corrected. (2) Several climate-model sensitivity experiments have been designed, executed, and analyzed. (3) Results have been described in the literature and at meetings.

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TITLE: Transport of Dissolved and Suspended Materials in Surface Waters

PROJECT NUMBER: NR 90—147

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

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

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

PROGRESS: Development of depth-averaged hydrodynamic models for use as the basis for transport modeling continued. A comparison of the vertically averaged hydrodynamic models TRIM (Cheng and Casulli) and SIMSYS2D (Leendertse) in several hypothetical cases showed that TRIM was very efficient but also quite dissipative (a problem in weakly forced systems) and that SIMSYS2D required a limited time step for accuracy, which limited its efficiency. In order to develop a more accurate, yet still efficient, code related to the semi-implicit method used in TRIM, codes were developed to solve the two-dimensional flow equations by a partial-block Gauss-Seidel iterative process. The scheme used in TRIM is a special case of such a process. Numerical schemes were developed to compare the use of the Eulerian-Lagrangian method in the partial-block process (no use, use for momentum only, use for mass and momentum). A literature review continued on the transport of dissolved and suspended materials in surface waters and on numerical methods for solving the relevant transport equations in two and three dimensions.

The capability of the two-dimensional, vertically averaged, finite-element model FESWMS—2DH to handle flooding and dewatering of elements was further improved. Development of a UNIX-based model output plotting system (MOPS) based on the Graphical Kernel System (GKS) and the Network Common Data Form (netCDF) continued. The completed system will be able to produce plots of input to and output from hydrodynamic/ transport models.

A cooperative data-collection effort was planned with personnel of the Florida District to provide data for the validation of two- and three-dimensional estuarine hydrodynamic/ transport models.

TITLE: Regional Water-Quality Assessment

PROJECT NUMBER: NR 90—148

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

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

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

PROGRESS: This is a new project established last year. Work has been initiated with the Delaware-Maryland-Virginia (Delmarva) project of the NAWQA Program to investigate network design issues associated with the surface-water ground-water studies and the use of multivariate statistical procedures to classify shallow ground-water quality and to relate the classifications to landscape features and surface-water characteristics. A course on the design of regional ground-water quality studies was developed for the Italian National Research

Council. Work is well underway on a text to be published by Van Nostrand Reinhold in 1992 entitled "Regional Ground-Water Quality."

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TITLE: Ice and Climate

PROJECT NUMBER: WR 70–064

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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: Sea Ice—Completed the processing and started the analysis of the winter Barents Sea air/ocean microwave observations acquired during the Seasonal Ice Zone Experiment (SIZEX)—1989. SIZEX is a European Space Agency (ESA) program, and the 1989 experiment was the key ocean/ice prelaunch experiment for the first European Research Satellite (ERS—1). Completed the science and operation plans for SIZEX—92, the post-launch ERS—1 experiment. Highlights of the joint USGS/CNES (French Space Agency) program include: (1) acceptance by

ESA of our proposal for the Franco-American TOPEX Satellite; (2) the processing and analysis of 3 years of Geosat global ocean sea state observations; and (3) CNES participation in SIZEX—92. Snow—The joint USGS/NASA/USDA passive microwave snow research program continues to demonstrate and develop new techniques for the remote sensing of snow from space. The NOAA National Operational Hydrologic Remote Sensing Center has begun using a snow cover passive microwave algorithm, developed by this project, to supplement the Center's snow cover products usually derived from standard visible observations. Using only the Scanning Multichannel Microwave Radiometer (SMMR) observations, this project has generated a snowpack climatology, from 1979 to 1986, for the Upper Colorado River Basin. We found that a spatial integral of the winter SMMR observations alone give a strong index of the following spring flow in the Colorado River. We continued to collect internal snowpack data from index sites in the basin. These data are being used to improve global snowpack estimates made from satellite observations. Ice Sheets—The first field season of the National Science Foundation (NSF) funded project to study the structure and evolution of, and interaction between, the West Antarctic Ice sheet (ALICE: Airborne Lithosphere and Icesheet Experiment), was successfully completed. A 10 kw ice-penetrating radar, a magnetometer, a gravity meter, and six precision navigation systems were installed in a Twin Otter aircraft and successfully test flown in Antarctica. Glaciers—At South Cascade Glacier, the 2-decade-long program of mass balance data continues, which has shown record negative mass balance for the past 3 years. At Hubbard Glacier, in cooperation with the Alaska District Office, we maintained camera sites and obtained sequential oblique photography of the terminus, and we have observed that the terminus is advancing rapidly. At Columbia Glacier, we continue to monitor the drastic retreat.

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

PROJECT NUMBER: WR 76—140

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

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

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

PROGRESS: This project continues to provide technical guidance and support to the Interagency study of San Francisco Bay/Delta. The project chief served as a technical advisor to overall hydrodynamic research, and Jeff Gartner provided technical advice and participated in the California District's field data collection program. The collaboration with the Australia Institute of Marine Science and the California District Office in 1990 revealed that the sediment dynamics in San Francisco Bay is extremely complex. Data analysis is still in progress. Preliminary results indicate that the data are highly variable. The high variability of data could be caused by relatively low sediment concentration (therefore high noise to signal ratio), large variations in a tidal cycle, and strongly three-dimensional structure of fine suspended sediment distribution. Further analysis of the data will be pursued to correlate the in situ measurements of fine suspended sediment concentration with back-scattered signals from an Acoustic Doppler Current Profiler. Significant progress has been made in both two-dimensional (2—D) and three-dimmensional (3—D) estuarine hydrodynamic modeling research. A two-dimensional, Tidal, Residual, and Intertidal Mudflat model (TRIM), was developed in collaboration with Professor Vincenzo Casulli of the University of Trento, Trento, Italy. The model has been tested at no fewer than six estuarine systems including detailed calibration and verification using an extensive data set of San Francisco Bay, Calif. A journal paper has been tentatively accepted for publication by Journal of Geophysical Research, Oceans, the revision of the paper has been sent to the journal editor. Pre- and post-processing programs for TRIM have been developed. This modeling system will be used in District estuarine programs, thus it contributes to technology transfer. Collaborating with Professor Casulli, we have made a new 3—D hydrodynamic model based on a semi-implicit numerical formulation. Preliminary evaluation of the model indicates that the model is extremely efficient. The efficiency of a large scale, three-dimensional model is a very important issue. Only models with high computational efficiency can be used to represent complex estuarine system for a long period of time. This model has such a potential.

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

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

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

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

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

TITLE: Analysis and Modeling of Conservative and Nonconservative Transport Processes

PROJECT NUMBER: WR 83–183

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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. Emphasis has been placed on salinity intrusion into the Delaware Bay and River, and the creation of a field-scale problem for testing numerical models.

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

PROJECT NUMBER: WR 84—187

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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 acid mine drainage St. Kevin Gulch (Colo.) tracer and hydrometric techniques have documented the existence of complex stream-watershed connections potentially altering solute transport. Improved assessments of watershed inflows to the stream have resulted from collaboration with the Center for Advanced Decision Support for Water and Environmental Systems (CADSWES) in Colorado to develop Colorado District capabilities for simulation analysis within the Modular Hydrologic Modeling System (Leadville, Colo.—Upper Arkansas River Toxic Substances Hydrology Site; Harvey, Zellweger, and Bencala working with McKnight, Kimball, Broshears, and Tate). Comparisons of multiple tracer injections in Little

Lost Man Creek, Calif., have documented bromide transport at a meter per hour through the inter-gravel zones of a substream channel and then export to the channel. (Orick, Calif.; Harvey, Zellweger, and Bencala working with Triska, Duff, and Jackman).

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SURFACE-WATER HYDROLOGY

TITLE: Fluvial Processes and River Mechanics

PROJECT NUMBER: WR 83—194

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

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

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

PROGRESS: Debris-flow research has progressed in theoretical and experimental phases. Significant results in the theoretical phase were the analytical expressions of theoretical velocity profiles for debris flow simulated in each of the conveyor-belt flume and the ring-shear apparatus based on a simplified version of the generalized viscoplastic fluid (GVF) model. The theoretical velocity profiles were then compared with measured ones from experiments, thereby evaluating the rheological parameters of a simulated debris flow. In the experimental phase, data acquired and analyzed from debris-flow experiments at the University of California--Berkeley were a few set of (1) measured velocity profiles and flow profiles with or without a snout in the conveyor-belt flume for dry flows of 5 or 14 mm glass spheres; and (2) measured velocity profiles, average shear and normal stresses on the shearing plane, and volume change, if any, of the tested sample in the ring-shear apparatus for dry flows of 3 or 5 mm glass spheres. Other areas of research in progress were: (1) the further evaluation of power laws for flow resistance in terms of Coles' wake law, (2) the formulation of criteria for free-surface instability based on the power law for flow resistance, (3) the two-phase flow theory applied to modeling stratified sediment gravity flow, and (4) the development of a "layered-flow" theory for gravity-induced granular flows.

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TITLE: Mathematical Modeling Principles

PROJECT NUMBER: WR 73—197

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

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

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

PROGRESS: Developed a new transport algorithm for sand and sand-gravel mixtures. The algorithm computes multiple-size transport, scour, fill, and armoring by allocating stream power to various pertinent processes in a hierarchial fashion. With the exception of those in the transport relations (such as the Ackers-White formula), the formulation is parameterless. Sensitivity analysis of the formulation indicates it to be appropriate for computing long-term sediment budgets in the Grand Canyon of the Colorado River. Secured funding for and commenced work on extensive study of geomorphology, sediment transport, beach evolution, water quality, and riparian ecology in Grand Canyon, Arizona.

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TITLE: Resolution of Hydroclimatic Uncertainty

PROJECT NUMBER: WR 89—201

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

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

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

PROGRESS: Basic research on the optimality of histograms has been conducted as a result of shortcomings in statistical theory that were elucidated in the development of a relative information measure for climate model outputs. Resolution of these shortcomings have delayed subsequent development and implementation of the relative information measure. A philosophical statement on the role of hydroclimatic uncertainty in the management of United States water resources was prepared for the U.S. National Research Council (NRC) and is to be published in the proceedings of an NRC workshop by the National Academy Press.

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APPENDIX

APPENDIX--*Alphabetical listing by Project Chief*

PROJECT CHIEF	DISCIPLINE	PROJECT NUMBER	PROJECT TITLE	PAGE
Alley, William	SW Hydrology	NR 90—148	Regional Water-Quality Assessment	281
Andrews, Edmund D.	Geomorphology and Sediment	CR 82—273	River Mechanics	73
Averett, Robert C.	Ecology	CR 88—312	Ecological Interactions of Lakes and Streams	15
Averett, Robert C. and Winter, Thomas C.	Ecology	CR 90—323	Interdisciplinary Research Initiative at the Shingobee Headwaters Research Area, Minn.	19
Back, William	GW Chemistry	NR 57—034	Spatial Distribution of Chemical Constituents in Ground Water	101
Baedecker, Mary Jo	GW Chemistry	NR 83—129	Comparative Study of Organic Degradation in Selected Hydrogeologic Environments	117
Baltzer, Robert A.	SW Hydrology	NR 69—019	Numerical Simulation of Hydrodynamic Processes in Rivers, Estuaries, and Coastal Embayments	263
Bencala, Kenneth E.	SW Hydrology	WR 84—187	Coupled Transport and Geochemical Processes Determining the Fate of Chemicals in Surface Waters	293
Bennett, James P.	SW Hydrology	WR 73—197	Mathematical Modeling Principles	298
Benson, Larry V.	SW Chemistry	CR 82—207	Arid Regions Climate and Chemistry	217

APPENDIX--*Alphabetical listing by Project Chief*—continued

PROJECT CHIEF	DISCIPLINE	PROJECT NUMBER	PROJECT TITLE	PAGE
Betancourt, Julio	Ecology	WR 76—145	Biotic Response to Climatic Variability and Human Impacts in arid lands	41
Bredehoeft, John D.	GW Hydrology	WR 75—176	Water Wells as Strain Meters	187
Bricker, Owen P.	SW Chemistry	NR 81—109	Geochemical Cycling of Trace Elements and Nutrients in Natural Water Systems	239
Brown, Charles E.	GW Hydrology	NR 84—130	Multivariate Statistical Techniques for Assessing Regional Ground-Water Quality and Quantity	171
Callender, Edward	SW Chemistry	NR 76—065	Sedimentary Geochemical Processes Affecting the Exchange of Nutrients and Transition Metals Between Sediment and Water in Riverine, Estuarine, and Lacustrine Environments	232
Campbell, W.J.	SW Hydrology	WR 70—064	Ice and Climate	283
Carter, Virginia P.	Ecology	NR 73-090	Remote Sensing and Ecological Research in Wetlands	21
Chen, Cheng-lung	SW Hydrology	WR 83—194	Fluvial Processes and River Mechanics	296
Cheng, Ralph T.	SW Hydrology	WR 76—140	Hydrodynamics and Mathematical Modeling of Circulation and Transport Phenomena in Tidal Estuaries	287
Chiou, Cary T.	GW Chemistry	CR 83—283	Environmental Dynamics of Persistent Organic Compounds	93

APPENDIX--*Alphabetical listing by Project Chief*—continued

PROJECT CHIEF	DISCIPLINE	PROJECT NUMBER	PROJECT TITLE	PAGE
Claassen, Hans C.	SW Chemistry	CR 75—189	Geochemical Kinetics Studies of Silicate Rock Hydrologic Systems	211
Cleveland, Jesse M.	GW Chemistry	CR 77—223	Transuranium Research	88
Cloern, James E.	Ecology	WR 79—164	Plankton Dynamics in Tidal Estuaries	45
Conomos, T. John	SW Hydrology	WR 77—156	Research Vessel Polaris Operations in San Francisco Bay and Adjacent Coastal Ocean	290
Constantz, James E.	GW Hydrology	WR 87—193	Temperature Effects in the Unsaturated Zone	197
Cooley, Richard L.	GW Hydrology	CR 76-191	Mathematical Simulation of Subsurface-Water Flow Using Uncertain and Incomplete Data	154
Coplen, Tyler B.	GW Chemistry	NR 75—064	Physical Chemistry of Stable Isotope Fractionation in Hydrologic Processes	110
Davis, James A., III	GW Chemistry	WR 70—065	Partitioning of Solutes between Solid and Aqueous Phases	125
Eberl, Dennis D.	GW Chemistry	CR 82—276	Geochemistry of Clay-Water Reactions	90
Emmett, William W.	Geomorphology and Sediment	CR 74—187	Hydraulics and Mechanics of Bedload-Transport Processes	68
Essaid, Hedeff I.	GW Hydrology	WR 89—199	The Fate and Transport of Immiscible Contaminants in the Subsurface	201

APPENDIX--*Alphabetical listing by Project Chief*—continued

PROJECT CHIEF	DISCIPLINE	PROJECT NUMBER	PROJECT TITLE	PAGE
Feder, Gerald L.	GW Chemistry	NR 79—132	Relationship Between Chemical Quality of Natural Waters and Human Health and Disease	119
Getzen, Rufus T.	GW Hydrology	WR 76—171	Hydrologic Analysis of Petrofabrics--Sandstones	186
Glenn, Jerry L.	Geomorphology and Sediment	CR 81—266	Transport and Deposition of Sediments and Sediment-Borne Contaminants in Tidal Rivers and Estuaries	71
Godsy, Edward M.	Ecology	WR 71-068	Fate of Organic Chemicals in Subsurface Environments	34
Goerlitz, Donald F.	GW Chemistry	WR 84—189	Chemistry of Aquatic Organic Matter	140
Goldberg, Marvin C.	SW Chemistry	CR 76—199	Water Chemistry of Sediment Surface Coatings	213
Gorelick, Steven M.	GW Hydrology	WR 82—178	Models for Ground-Water Management	189
Grove, David B.	SW Hydrology	NR 88—143	Research Vessel Leopold Operations in Potomac River, Chesapeake Bay, and Adjacent Coastal Waters	276
Grove, David B.	GW Hydrology	NR 73—139	The Mathematical Simulation of the Transport and Reaction of Chemical Species in Ground Water	175
Harvey, Ronald W.	Ecology	WR 86-191	Interaction of Bacteria with Environmental Contaminants and Solid Surfaces in the Aquatic Environment	57

PROJECT CHIEF	DISCIPLINE	PROJECT NUMBER	PROJECT TITLE	PAGE
Hem, John D.	SW Chemistry	WR 57—076	Chemistry of Hydrosolic Metals and Related Constituents of Natural Water	245
Herkelrath, William N.	GW Hydrology	WR 82—179	Nonisothermal Multiphase Flow	191
Hsieh, Paul A.	GW Hydrology	WR 83—184	Hydrology of Fractured Rocks	195
Hupp, C.R.	Ecology	NR 90—145	Vegetation and Hydrogeomorphic Relations	27
Ingebritsen, Steven E.	GW Hydrology	WR 74—121	Hydrologic Studies of Heat and Mass Transport	181
James, Ronald V.	GW Chemistry	WR 68—036	Factors Determining Solute Transfer in the Unsaturated Zone	123
Jarrett, Robert	SW Hydrology	CR 90-321	Paleohydrology and Climate Change	261
Jones, Blair F.	GW Chemistry	NR 69—020	Mineral-Water Interaction in Saline Environments	98
Kendall, Carol	GW Chemistry	WR 91—080	Stable Isotope Tracers of Biogeochemical and Hydrologic Processes	128
Kharaka, Yousif K.	GW Chemistry	WR 76—139	Geochemistry of Water in Fine Grained Sediments	134
Kipp, Kenneth L.	GW Hydrology	CR 85—292	Ground-Water Solute-Transport Simulation	159
Konikow, Leonard F.	GW Hydrology	NR 81—120	Digital Modeling of Transport in the Saturated Zone	168

APPENDIX--*Alphabetical listing by Project Chief*—continued

PROJECT CHIEF	DISCIPLINE	PROJECT NUMBER	PROJECT TITLE	PAGE
Kraemer, Thomas F.	GW Chemistry	NR 82—138	Uranium-Thorium Series Radioisotopes in Ground-Water and Surface-Water Systems	121
Kuwabara, James S.	Ecology	WR 86—190	Solute Transport Involving Biological Processes in Surface Waters	54
LaBaugh, James W.	Ecology	CR 85—293	The Role of Chemical Fluxes in the Biogeochemistry of Inland Surface Waters, Including Lakes Reservoirs, and Wetlands	10
Lai, Vincent C.	SW Hydrology	NR 79-096	Computational Hydraulics for Surface Water Problems	266
Landa, Edward R.	SW Chemistry	NR 78—092	Hydrogeochemical Controls on the Migration of Radionuclides from Uranium Mill Tailings	235
Landwehr, Jurate M.	SW Hydrology	NR 84-133	Regional Hydrologic Processes	274
Leavesley, George H.	SW Hydrology	CR 77—228	Precipitation-Runoff Modeling of Watershed System	252
Lee, Jonathan	SW Hydrology	NR 90—147	Transport of Dissolved and Suspended Materials in Surface Waters	279
Leenheer, Jerry A.	SW Chemistry	CR 84—285	Comprehensive Organic Analysis of Water	226
Leland, Harry V.	Ecology	WR 75-137	Effects of Toxic Substances on Aquatic Communities	39

PROJECT CHIEF	DISCIPLINE	PROJECT NUMBER	PROJECT TITLE	PAGE
Lovley, Derek R.	Ecology	NR 87-136	Modeling of Microbially Catalyzed Geochemical Reactions in Aquatic Environments	24
Luoma, Samuel N.	Ecology	WR 75—125	Availability of Trace Elements in Sediments to Aquatic Organisms	36
Malcolm, Ronald L.	SW Chemistry	CR 68—046	Origin, Characterization, and Quantification of Natural Organic Solutes in Water	204
Mariner, Robert H.	GW Chemistry	WR 79—165	Chemical and Isotope Studies of Thermal Waters of the Western United States	137
McKnight, Diane M.	Ecology	CR 84-286	Interactions Between Organic Solutes and Trace Metals in Natural Waters, and Their Ecological Role	6
Meade, Robert H.	Geomorphology and Sediment	CR 75—102	Movement and Storage of Sediment in River Systems	64
Meade, Robert H.	Geomorphology and Sediment	CR 87—309	Sediment-Transported Pollutants in the Mississippi River	76
Milly, Chris D.	SW Hydrology	NR 88—144	Continental Hydrology and Global Climate	277
Moench, Allen F.	GW Hydrology	WR 75—127	Analytical Modeling of Flow and Transport in Aquifers and Geothermal Reservoirs.	184
Moss, Marshall E.	SW Hydrology	WR 89—201	Resolution of Hydroclimatic Uncertainty	299
Naff, Richard L.	GW Hydrology	CR 90—319	Application of Stochastic Processes in Hydrogeology	162

APPENDIX--*Alphabetical listing by Project Chief*—continued

PROJECT CHIEF	DISCIPLINE	PROJECT NUMBER	PROJECT TITLE	PAGE
Neuzil, Christopher E.	GR Hydrology	NR 81—035	Hydrologic Behavior of Cretaceous Shales	164
Nichols, Frederic H.	Ecology	WR 86—192	Environmental Influences on Estuarine Benthic Community Dynamics	60
Nimmo, John R.	GW Hydrology	WR 89—198	Physical Characteristics that Determine Flow in the Unsaturated Zone	199
Nordstrom, Darrell K.	GW Chemistry	WR 75—128	Chemical Modeling and Thermodynamic Data Evaluation of Major and Trace Elements in Acid Mine Waters and Ground Waters	131
Oremland, Ronald S.	Ecology	WR 81—174	Microbial Biogeochemistry of Aquatic Environments	48
Osterkamp, Waite R.	Geomorphology and Sediment	CR 79—311	Sediment Impacts from Disturbed and Undisturbed Lands	78
Paillet, Frederick L.	GW Hydrology	CR 64—140	Borehole Geophysics as Applied to Geohydrology	150
Parkhurst, David L.	GW Chemistry	CR 89—318	Reaction-Transport Modeling in Ground-Water systems	96
Pereira, Wilfred E.	SW Chemistry	WR 83—204	Origin, Fate, and Transport of Organic Compounds in Surface and Ground Waters and Their Effect on Water Quality	248
Peterson, David H.	Ecology	WR 68-046	Geochemistry of Riverine and Estuarine Waters	31
Plummer, L. Niel	GW Chemistry	NR 76—056	Kinetics and Thermodynamics of Chemical Evolution in Ground-Water Systems	106

APPENDIX--*Alphabetical listing by Project Chief*—continued

PROJECT CHIEF	DISCIPLINE	PROJECT NUMBER	PROJECT TITLE	PAGE
Rathbun, Ronald E.	SW Hydrology	CR 77—301	Transport and Degradation of Organic Substances in Streams	258
Reddy, Michael M.	SW Chemistry	CR 83—284	Corrosion of Building Materials as Determined From Solid Weathering Products Removed by Wet Precipitation	223
Rubin, Jacob	GW Hydrology	WR 82—180	Theories of Water Flow and of Solute Transport in the Unsaturated Zone	193
Schaffranek, Raymond W.	SW Hydrology	NR 80—104	Simulation Modeling of Hydrodynamic Systems	268
Seeley, James	SW Chemistry	CR 89—316	Solid Phase Chemistry and Related Environmental Processes	230
Shapiro, Allen M.	GW Hydrology	NR 84—134	Transport Phenomena in Fractured Rock	173
Simon, Nancy S.	SW Chemistry	NR 86—135	Distribution and Speciation of Metals in Sedimentary Environments	242
Slack, Keith V.	Ecology	WR 61—012	Limnology: Controls on Distribution and Composition of Benthic Communities of Inland Aquatic Ecosystems	29
Smith, Richard L.	Ecology	CR 86—295	Microbial Transformation of Dissolved Organic Carbon in Aquatic Environments	12
Sorey, Michael L.	GW Hydrology	WR 72—108	Technical Coordination and Support of WRD Geothermal Studies	180

PROJECT CHIEF	DISCIPLINE	PROJECT NUMBER	PROJECT TITLE	PAGE
Sorey, Michael L.	GW Hydrology	WR 73—102	Modeling and Monitoring Heat and Fluid Flow in Geothermal Systems	178
Stallard, Robert F.	Geomorphology and Sediment	CR 88-313	Sediment-Water Chemistry in Large River Systems: Biogeochemical, Geomorphic, and Human Controls	81
Stonestrom, David A.	GW Hydrology	WR 63—024	Application of the Unsaturated Flow Theory to the Phenomena of Infiltration and Drainage	176
Striegl, Robert G.	Ecology	CR 91—320	Characterization of Biotic and Biogeochemical Interactions at Environmental Interfaces	17
Sundquist, Eric T.	SW Chemistry	NR 79—099	Carbon Fluxes in Hydrologic and Geologic Processes	237
Tasker, Gary D.	SW Hydrology	NR 82—125	Hydrologic Regression and Data-Network Design in Coal Mining Regions	271
Taylor, Howard E.	SW Chemistry	CR 83—282	Research in Analytical Environmental Trace Element Chemistry and Its Impact on Water Quality	220
Thorstenson, Donald C.	GW Chemistry	NR 79-093	Chemical Models of Natural Systems	113
Triska, Frank J.	Ecology	WR 84—186	Biotic Interface with Fluvial Transport: Processes Associated with Dissolved Solutes in Transport	51
Troutman, Brent M.	SW Hydrology	CR 83—279	Statistical Analysis of Errors in Hydrologic Models	255

APPENDIX--*Alphabetical listing by Project Chief*—continued

PROJECT CHIEF	DISCIPLINE	PROJECT NUMBER	PROJECT TITLE	PAGE
Voss, Clifford I.	GW Hydrology	NR 78—089	Investigations of Single and Multiphase Fluid Flow, Mass and Energy Transport, and Fluid Phase Change in the Subsurface Environment	166
Walters, Roy A.	SW Hydrology	WR 83—183	Analysis and Modeling of Conservative and Nonconservative Transport Processes	291
Webb, Robert H.	Geomorphology and Sediment	WR 89-200	Response of Fluvial Systems to Climatic Variability	84
Weeks, Edwin P.	GW Hydrology	CR 69—200	Field Applications of Unsaturated Zone Flow Theory	156
Wershaw, Robert L.	SW Chemistry	CR 68—132	Behavior of Natural Polyelectrolytes in Water	207
White, Arthur F.	GW Chemistry	WR 88—196	Geochemical Reactions Between Water and Mineral Substrates	143
Williams, Garnett P.	Geomorphology and Sediment	CR 65—105	Effects of Water and Sediment Discharges on Channel Morphology	66
Winograd, Isaac J.	GW Chemistry	NR 74—041	Interface of Paleoclimatology and Aquifer Geochemistry	104
Winter, Thomas C. and Averett, Robert C.	Ecology	CR 90-323	Interdisciplinary Research Initiative at the Shingobee Headwaters Research Area, Minnesota	19
Winter, Thomas C.	GW Hydrology	CR 74—090	The Role of Lakes in the Hydrologic System, with Emphasis on Their Relation to Ground Water	148

PROJECT CHIEF	DISCIPLINE	PROJECT NUMBER	PROJECT TITLE	PAGE
Wood, Warren W.	GW Chemistry	NR 81—122	Dispersion of Toxic and Radioactive Wastes in Ground-Water Systems	115