U.S. GEOLOGICAL SURVEY TOXIC WASTE—GROUND-WATER CONTAMINATION PROGRAM—FISCAL YEAR 1983

By Stephen E. Ragone

U.S. GEOLOGICAL SURVEY

OPEN-FILE REPORT 84-474

Reston, Virginia
1984

UNITED STATES DEPARTMENT OF THE INTERIOR

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SI UNITS AND INCH-POUND SYSTEM EQUIVALENTS

[SI, International System of Units, a modernized metric system of measurement. All values have been rounded to four significant digits except 0.01 bar, which is the exact equivalent of 1 kPa. Use of hectare (ha) as an alternative name for square hectometer (hm^2) is restricted to measurement of land or water areas. Use of liter (L) as a special name for cubic decimeter (dm^3) is restricted to the measurement of liquids and gases; no prefix other than milli should be used with liter. Metric ton (t) as a name for megagram (Mg) should be restricted to commercial usage, and no prefixes should be used with it. Note that the style of meter^2 rather than square meter has been used for convenience in finding units in this table. Where the units are spelled out in text, Survey style is to use square meter]

SI unit		Inch-Pound equivalent	
Length			
millimeter (mm)	=	0.039 37	inch (in)
meter (m)	=	3.281	feet (ft)
	=	1.094	yards (yd)
kilometer (km)	=	0.621 4	mile (mi)
	=	0.540 0	mile, nautical (nmi)
Area			
centimeter^2 (cm^2)	=	0.155 0	inch^2 (in^2)
meter^2 (m^2)	=	10.76	feet^2 (ft^2)
	=	1.196	yards^2 (yd^2)
	=	0.000 247 1	acre
hectometer^2 (hm^2)	=	2.471	acres
	=	0.003 861	section (640 acres or 1 mi^2)
kilometer^2 (km^2)	=	0.386 1	mile^2 (mi^2)
Volume			
centimeter^3 (cm^3)	=	0.061 02	inch^3 (in^3)
decimeter^3 (dm^3)	=	61.02	inches^3 (in^3)
	=	2.113	pints (pt)
	=	1.057	quarts (qt)
	=	0.264 2	gallon (gal)
	=	0.035 31	foot^3 (ft^3)
meter^3 (m^3)	=	35.31	feet^3 (ft^3)
	=	1.308	yards^3 (yd^3)
	=	264.2	gallons (gal)
	=	6.290	barrels (bbl) (petroleum, 1 bbl = 42 gal)
	=	0.000 810 7	acre-foot (acre-ft)
hectometer^3 (hm^3)	=	810.7	acre-feet (acre-ft)
kilometer^3 (km^3)	=	0.239 9	mile^3 (mi^3)
Volume per unit time (includes flow			
decimeter^3 per second (dm^3/s)	=	0.035 31	foot^3 per second (ft^3/s)
	=	2.119	feet^3 per minute (ft^3/min)
Volume per unit time (includes flow)—Continued			
decimeter^3 per second (dm^3/s)	=	15.85	gallons per minute (gal/min)
	=	543.4	barrels per day (bbl/d) (petroleum, 1 bbl = 42 gal)
meter^3 per second (m^3/s)	=	35.31	feet^3 per second (ft^3/s)
	=	15 850	gallons per minute (gal/min)
Mass			
gram (g)	=	0.035 27	ounce avoirdupois (oz avdp)
kilogram (kg)	=	2.205	pounds avoirdupois (lb avdp)
megagram (Mg)	=	1.102	tons, short (2 000 lb)
	=	0.984 2	ton, long (2 240 lb)
Mass per unit volume (includes density)			
kilogram per meter^3 kg/m^3)	=	0.062 43	pound per foot^3 (lb/ft^3)
Pressure			
kilopascal (kPa)	=	0.145 0	pound-force per inch^2 (lbf/in^2)
	=	0.009 869	atmosphere, standard (atm)
	=	0.01	bar
	=	0.296 1	inch of mercury at 60°F (in Hg)
Temperature			
temp kelvin (K)	=	[temp deg Fahrenheit (°F)+459.67]/1.8	
temp deg Celsius (°C)	=	[temp deg Fahrenheit (°F)−32]/1.8	

ABSTRACT

The report describes the research being conducted as part of the Toxic Waste--Ground-Water Contamination Program of the U.S. Geological Survey. Descriptions are provided of the process-oriented research being conducted on ground-water hydrology, inorganic and organic geochemistry, and ecology. Problem-oriented research is described for three sites where ground-water contamination has resulted from a crude oil pipeline break near Bemidji, Minnesota; the infiltration of sewage plant effluent on Cape Cod, Massachusetts; and the infiltration of creosote and pentachloraphenol from a waste disposal pit at Pensacola, Florida. Site studies provide the opportunity to evaluate and improve our understanding of earth-science processes in the complex multiphase, multicomponent systems found in nature. Results from the field studies should have transfer value to other sites affected by similar types of contaminants.

The unsaturated zone and surface waters often are impacted by contaminants transported through the subsurface. Thus, some process- and problem-oriented research of these systems is being conducted in order to evaluate their effect on ground-water transport of contaminants. Descriptions of the studies are included in the report.

A brief overview is given for regional ground-water quality studies which are in the formative stages.

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TOXIC WASTE—GROUND-WATER CONTAMINATION PROGRAM
FISCAL YEAR 1983

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INTRODUCTION

Ground-water contamination resulting from the planned or inadvertent disposal of wastes or from certain land-use practices is one of the most publicized environmental issues of the 1980's. Estimates suggest that only about 1 percent of the Nation's ground water has been contaminated. However, ground-water contamination has affected the drinking water supplies of millions of people and has also degraded the water quality in numerous shallow aquifer systems that recharge surface-water systems.

Ground-water contamination can be, by virtue of the nature of the resource, an insidious problem. Because of the relatively slow rate of movement of ground water, typically on the order of several feet per day to several feet per year, instances of ground-water contamination may not be discovered for years to tens of years after the contaminants are disposed. Many instances of contamination are discovered only after a drinking water supply is affected.

Although it is reassuring that only a relatively small volume of ground water is estimated to be contaminated, the estimated tens of thousands of waste facilities that leak hundreds of billions of gallons of liquids into the ground each year have the potential to seriously degrade the resource. Furthermore, pesticides currently in use often have low-soil affinity and high persistence that allows them to reach ground water.

A question that remains to be answered is how the wastes are affecting the usefulness of the ground-water resources throughout the Nation. Currently, there is limited quantitative understanding of the extent or degree of ground-water contamination in the United States, and there is an insufficient understanding of the kinds of physical, chemical, and microbiological processes that affect the fate of contaminants as they move through the subsurface.

The U.S. Geological Survey (USGS) has a long-standing involvement in the study of the quality and quantity of the Nation's water resources through research, areal investigations, and data-collection activities. In fiscal year (FY) 1982, the Toxic Waste—Ground-Water Contamination Program was initiated to better focus research and field studies on toxic waste—ground-water contamination issues. Using the data bases and experiences of past USGS work which are specifically relevant to the problem, this program will provide earth-science information that will help to protect ground-water resources. The research being conducted by the Toxic Waste Program has relevance to other research programs in the USGS. The program is closely coordinated with other programs of the Geological Survey—Radioactive Waste Disposal, Regional Aquifer-Systems Analyses, the Federal-State Cooperative Program, and studies of glacial deposits in the eastern United States. In some cases, funds from these studies provide partial support for the projects described in this report.

The purpose of this report is to provide to the technical community a summary of the Toxic Waste—Ground-Water Contamination research program of the USGS. It is hoped that the description of the major research studies will lead to better communication within the technical community and the exchange of scientific information.

PROCESS-ORIENTED RESEARCH

Physical, chemical, and microbiological processes affect the transport of contaminants through the subsurface. The objective of the process research being conducted as part of the Toxic Waste Program is to develop a sufficiently good understanding of the controlling processes in order to predict contaminant fate.

Both the unsaturated zone and surface waters can be affected by contaminants transported through the subsurface. Thus, some study of processes occurring in the unsaturated zone and in surface waters is necessary in order to evaluate their impact on ground-water transport of contaminants. Descriptions of these studies are included in the following sections.

Projects, which are grouped by the major disciplines of ground-water hydrology, organic geochemistry, ecology, and inorganic geochemistry, are described briefly on the following pages. Also given is the name of the project chief and recent publications resulting from the project.

Ground-Water Hydrology

Ground-water hydrology provides a quantitative understanding of the flow of water and the transport of its constituents through the subsurface. The classical definition of ground water defines it as water that occurs in fully saturated, consolidated, and unconsolidated earth materials. However, it is important that the unsaturated zone also be studied because of the number and complexity of processes occurring there which can affect the transport of hazardous substances to the water table.

As a discipline, ground-water hydrology includes the mathematical, chemical, geological, and physical sciences. Although there are many numerical methods available to help solve the mathematical problems associated with the description of flow and transport, many of problems require further study, and new methods need to be developed and tested:

- Hydrodynamic dispersion—The movement of solutes can be greatly affected by physical dispersion. Dispersion under natural conditions can be 1,000 to 10,000 times greater than that measured in the laboratory. Although it is possible to estimate an asymptotic value for dispersivity (the value approached after a relatively long distance of flow) from the statistical properties of hydraulic conductivity, there is no consensus about quantifying dispersion before it reaches the asymptotic value.

- Multiple phase flow—The transport of chemical constituents can occur as a gas or a liquid phase separate from the water phase. Quantitative methods are required to account for multiphase transport.

- Fracture flow—The highly heterogeneous nature of fractured-rock systems requires extension of classical approaches used to describe flow through porous media. Flow through fractured rock can be approached by aggregating the flows occurring through individual fractures or by determining a statistical value for the fractured rock mass.

- Unsaturated zone flow and transport—Ground-water quality can be significantly affected by chemical and solute dispersion processes in the unsaturated zone. Study is needed of how water content and mineral surfaces in the unsaturated zone may affect transport.

- Chemical and microbiological reactions—Simple chemical reactions currently can be included in the transport equation, but only after making simplifying assumptions. Studies of the chemical and microbiological processes affecting ground-water transport are described in later sections.

- Use of surface geophysical methods to characterize geohydrology and the extent of contamination—traditionally, geohydrologic information used to create mathematical models, was obtained by analyzing the aquifer material collected when wells were emplaced and by water level measurements made through the finished well. Although analyses of well records and well data remain an essential part of ground-water studies, other methods are being sought that will help locate plumes of hazardous substances by indirect means, so that contact with the hazardous substances can be minimized and so that plume geometry can be better delineated before embarking upon a costly and time-consuming drilling program. Surface geophysical methods can provide a relatively quick and inexpensive indirect method to characterize hydrogeologic setting and determine the 3-dimensional distribution of leachate plumes. However, the utility of this methodology requires that additional field studies be conducted in a variety of hydrogeologic settings.

The following projects address these research problems.

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

PROJECT CHIEF: Grove, David B.

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

OBJECTIVE: (1) Demonstrate the applicability of numerical modeling techniques to predict water-quality changes during transport of solutes through the saturated ground-water systems, and (2) predict the effects of chemical and physical stresses on the quality of ground water.

APPROACH: The mass-transport equation will be solved through numerical means using finite difference and finite element methods to produce a water-quality model that will predict the effects of chemical disturbances on the ground-water system. Field data and laboratory experiments will be used to verify the model.

REPORTS PUBLISHED:

Grove, D. B., 1982, Modeling the movement of contaminants in saturated ground-water systems, in The impact of waste storage and disposal on ground-water resources, Novitski, R. P., ed., Ithaca, New York, June 28-July 1, 1982, Proceedings, Center for Environmental Research, Cornell University, Ithaca, New York.

Grove, D. B., and Kipp, K. L., 1981, Modeling contaminant in porous media in relation to nuclear-waste disposal: A review in modeling and low-level waste management: An Interagency Workshop, Denver, Colorado, December 1-4, 1980, Proceedings: National Technical Information Service, p. 43-64.

Stollenwerk, K. G. and Grove, D. B., 1983, Adsorption and desorption of chromate in an alluvial aquifer near Telluride, Colorado (abs.): Agronomy Abstracts, American Society of Agronomy.

TITLE: Hydrology of Fractured Rocks

PROJECT CHIEF: Hsieh, Paul A.

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

OBJECTIVE: (1) Develop a comprehensive methodology of hydraulic testing in fractured rocks, and (2) investigate the relationship between hydraulic properties measured on different scales by characterizing the heterogeneity and anisotropy of the rock mass.

APPROACH: The theory and application of hydraulic testing methods will be developed to determine hydraulic properties of fractured rocks. Geologic and geophysical information will serve as background for designing single-hole and cross-hole packer tests. The effects of scale will be investigated by computer simulation using stochastic and geostatistical techniques. The results of small-scale field tests will be used to predict rock characteristics on larger scale systems.

TITLE: Factors Determining Solute Transfer in the Unsaturated Zone

PROJECT CHIEF: James, Ronald V.

PROBLEM: The quality of ground and surface waters often is significantly influenced by chemical and solute dispersion processes of the unsaturated zone. Frequently, it is impossible to predict these influences, because the effects of changes in water content or in the nature of solid surfaces are imperfectly understood and because the current transport modeling methods may not be well adapted to the situations encountered in practice.

OBJECTIVE: (1) Develop and test experimental theories and mathematical models of reacting-solute transport, so as to enhance the usefulness of such theories and models in assessing the impact of the unsaturated zone on water resources and environment quality, and (2) study chemical reactions involving radioactive nuclides as well as reactions of certain solutes found in industrial and agricultural effluents.

APPROACH: Mathematical models will be developed to aid the prediction of the transport of reacting solutes through porous media or at media boundaries. Studies will be conducted under a variety of conditions such as: (1) water-saturated systems with slow, steady water flows that involve a single, essentially equilibrium-controlled chemical reaction, or (2) steady but unsaturated flows, and fast, perhaps transient flows that involve kinetic-controlled reaction. Ground-water pollutant-management models will be developed that combine numerical simulation models and management techniques such as linear programming. Initial work will focus upon pollutant-source management in transient 1-dimensional systems with linear chemistry. Subsequent investigations will deal with pollutant-source management in 2-dimensions with nonlinear one-component chemical systems. The work will utilize existing simulation models and management models in hope of enhancing joint management and simulation capabilities.

TITLE: Digital Modeling of Transport in the Saturated Zone

PROJECT CHIEF: Konikow, Leonard F.

PROBLEM: Management of ground-water resources requires that the extent and rate of movement of contaminants in the saturated and unsaturated zones be understood. Although the basic mathematical transport models for ground-water systems have been developed, many of the parameters in these models have not been adequately investigated. Understanding of the physical and chemical processes that affect the fate of contaminants and mathematical models derived from this understanding must be validated and documented.

OBJECTIVE: (1) Increase understanding of the factors influencing the parameters in transport models and of the interrelationship between parameters, (2) use of this understanding to develop appropriate 2-dimensional and 3-dimensional mathematical models to describe contaminant movement in complex field situation including the unsaturated zone where critical, and (3) study appropriate digital computer algorithms used to numerically approximate the solution to the transport equations.

APPROACH: The particular numerical model which will be ultimately developed through this project will depend on choices of ground-water system complexities which are simulated and on the contaminant characteristics introduced to a system. Emphasis will be placed on those systems and contaminants for which transport model needs seem most critical. This emphasis will dictate the order in which particular models are initiated. The accuracy and efficiency of the analytical solutions, other numerical methods, and observed data from practical field problems.

REPORTS PUBLISHED:

Konikow, L. F. and Thompson, D. W., 1984, Ground-water contamination and aquifer reclamation at the Rocky Mountain Arsenal, Colorado, in Ground-water Contamination: Studies in Geophysics, National Academy Press, Washington, D.C., p. 93-103.

TITLE: Application of Surface Geophysical Techniques to Toxic-Waste Studies

PROJECT CHIEF: Olhoeft, Gary R.

PROBLEM: Many toxic-waste sites currently exist from past dumping in which the 3-dimensional distribution of the wastes is unknown. Non-invasive, non-destructive surface geophysical techniques can be used to elucidate the depth and areal extents of the waste as well as information about near surface geological interactions and migration. Inserting this information into geological, geochemical, and hydrological models could aid in the prediction of future migration of the waste.

OBJECTIVE: (1) Determine the utility of surface geophysical methods to measure the depth and areal extent of toxic waste and its interaction with the aquifer, and (2) evaluate the utility of surface geophysical methods to monitor in-situ geochemical reactions between waste components and between waste and the rock matrix.

APPROACH: Test, at several field sites, existing state-of-the-art geophysical techniques. Specifically, test induction loop-loop electromagnetics for detection of conductivity anomalies due to the presence of waste; test the spontaneous polarization technique as a monitor of ground-water flow; test complex resistivity to detect and monitor clay-organic reactions in situ; test ground penetrating radar for detailed interpretation of near-surface hydrologic conditions and for stratigraphic mapping.

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

PROJECT CHIEF: Wood, Warren W.

PROBLEM: The movement of toxic and radioactive substances in ground waters is principally the result of advection. However, the movement of solutes can be greatly affected by physical dispersion, ion exchange, mineral solution and precipitation, and ion filtration. Without knowledge of how these physical and geochemical factors affect the movement of hazardous substances, the prediction of their concentrations with time and space in an aquifer is highly uncertain.

OBJECTIVE: Develop field methods and techniques to measure critical physical and geochemical parameters which affect the movement of hazardous substances through regional ground-water systems.

APPROACH: Field methods and techniques will be used in naturally stressed systems. Through these studies, the importance of the various hydrogeologic and geochemical factors will be defined and the means will be studied to measure the magnitude of each.

REPORTS PUBLISHED:

Wood, Warren W., 1981, A geochemical method of determining dispersivity in regional ground-water systems: Journal of Hydrology, v. 54, no. 54, pp. 209-224.

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

PROJECT CHIEF: Voss, Clifford I.

PROBLEM: The subsurface environment is subject to both natural and man-imposed stresses, the interaction of which determines both its preservation and its use as a resource for water supply, energy production, and subsurface storage of energy and materials. Subsurface problems of current interest include: geothermal energy development, thermal and mechanical energy storage in aquifers and tunnels, radioactive-waste isolation, ground-water development in permafrost regions, pollution of ground water, and saltwater encroachment in aquifers. Study of these various problems is unified by the theoretical framework of the physics of single and multiphase fluid flow, mass, and energy transport and fluid phase change as applied to the subsurface environment.

OBJECTIVE: (1) Develop quantitative methods for the analysis of single and multiphase fluid flow, mass and energy transport and fluid phase change in the subsurface, and (2) apply these methods to field problems in order to illuminate hydrological relationships that are important in both the preservation and optimal employment of the subsurface.

APPROACH: A mathematical description of single or multiphase flow, transport and phase change processes will be developed. Analytical and/or numerical solutions of the mathematical description will be based on either hypothetical or field problem conditions. Simulation models and analytical methods for general classes of subsurface problems will be byproducts of the investigations.

Organic Geochemistry

Organic geochemistry provides an understanding of the fate of organic substances in natural hydrologic systems. In some cases, organic geochemical processes directly or indirectly affect the transport of inorganic substances as well. The research projects included in this section will help to:

- Develop methodologies that are useful in characterizing organic compounds.
- Describe the types of organic solutes found in natural and chemically stressed ground-water systems.
- Determine the structure of organic compounds and their reactivity with respect to other organic compounds, inorganic compounds and earth materials.
- Develop models to help describe organic-rich, ground-water environments.

TITLE: Comparative Study of Organic Degradation in Selected Hydrogeologic Environments

PROJECT CHIEF: Baedecker, Mary Jo

PROBLEM: Degradation of organic material produces organic compounds that both alter the quality of ground water and affect inorganic reactions. The hydrogeologic controls on organic-inorganic reactions and their rate are not well understood.

OBJECTIVE: The overall objective is to increase our understanding of reactions in ground-water systems that involve organic matter. Particular objectives are: (1) identification of organic and inorganic compounds that are present in ground water as a result of the degradation of organic material, (2) study the interaction of organic compounds with soils and aquifer materials, and (3) develop geochemical models to describe organic-rich ground water environments.

APPROACH: Several organic-rich ground-water environments 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 aquifer materials, the migration of organic compounds through the subsurface, the fractionation of isotopes and generation of gases, and the fate of inorganic constituents in association with organic materials.

TITLE: Environmental Dynamics of Persistent Organic Compounds

PROJECT CHIEF: Chiou, Cary T.

PROBLEM: The transport characteristics of the compounds across environmental phases are only qualitatively understood. Quantification of process rates and partition constants of organic pollutants in air, ground and surface water, soil, and biota is an important step in defining the level of contaminants in environmental media and the pathways of chemical exposure to man.

OBJECTIVE: The overall objectives are to delineate and quantify the processes affecting the movement and distribution of persistant organic solutes in environmental systems including soils, the unsaturated zone, and ground water. Specific objectives are: (1) determine the sorptive capacity of soil and sediment, (2) specify the roles of organic matter, mineral components, and moisture content or the sorption process, and (3) establish the physical basis of bioaccumulation of organic solutes from water.

APPROACH: The thermodynamic properties of the compounds and soil constituents will be used to determine the sorption of various organic compounds from water. Sorption from vapor phase will be determined to illustrate the effect of soil moisture content on sorptive process and capacity. The partition coefficients of solutes between lipid and water will be studied.

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

PROJECT CHIEF: Malcolm, Ronald L.

PROBLEM: Greater than 90 percent of the organic solutes in water are of natural origin, yet little is known about the chemistry or source of these organic materials. However, these substances are known to complex and solubilize trace metals, pesticides, and organic contaminant compounds; to increase the water solubility of hydrophobic toxic and contaminant solutes; to effect the vapor transport of simple organic compounds; and to serve as a food source for aquatic organisms. All these processes which have an effect upon surface- and ground-water quality, the distribution and movement of contaminant organic and inorganic compounds in compounds in surface and ground waters, as well as the esthetic value of water must be further clarified and quantified.

OBJECTIVE: The overall objectives are to quantify and to identify organic solutes that affect water quality. Specific objectives are to: (1) measure the amount of different organic solutes in various hydrologic environments, (2) understand the origin, structure, and reactivity of aquatic humic substances in ground and surface waters; (3) predict the processes which affect the fate and movement of natural and contaminant organic solutes in contaminated and uncontaminated surface and subsurface environments; (4) predict the organic association of small contaminant organic solutes with natural humic substances; and (5) elucidate the roles of natural organic solutes in water purification: reverse osmosis, chlorination, activated charcoal, and ozonation.

APPROACH: Intensive sampling will be conducted in uncontaminated and contaminated ground water to determine its composition and to provide baseline information of potential future contamination. Streams will be sampled to determined climatic, geologic, and seasonal variations in natural organic substances. Organic matter will be characterized from surface and ground water, soils, and plants in wetland environments to determine origin and source. From the characterization of natural organic matter, correlate and predict the amount and variety of chlorinated compounds in water.

REPORTS PUBLISHED:

Malcolm, R. L., Aiken, G. R., and Thurman, E. M., 1981, Hydrophilic organic solutes as tracers in ground-water recharge studies, Chap. 5 of American Chemical Society Environmental Division Symposium on Contaminants and Sediments, Honolulu, Hawaii: Journal of Chromatography, v. 2, p. 69-87.

Thurman, E. M., Wershaw, R. L., Malcolm, R. L., and Pinckney, D. J., 1982, Molecular size of aquatic humic substances. Organic Geochemistry, v. 4, p. 27-35.

Malcolm, R. L., 1982, Characterization of the types of organic substances in ground waters, Symposium on Water Quality Impacts of Deep Percolation, Arizona Department of Natural Resources, Scottsdale, Arizona, October 26, 1982.

TITLE: Origin, Fate, and Transport of Hazardous Wastes in the Subsurface Environment

PROJECT CHIEF: Pereira, Wilfred E.

PROBLEM: A large number of hazardous organic compounds derived from industrial, agricultural, and domestic sources have become a major problem in the management of ground-water resources. The problem is compounded by the complex behavior of organic contaminants and a lack of knowledge of fundamental processes governing their fate and transport in the subsurface environment. New analytical techniques are needed to measure refractory organic compounds in complex mixtures so that meaningful information on their origin, fate, and transport in the subsurface environment can be obtained.

OBJECTIVE: (1) Develop new analytical methodology to analyze selected refractory organic compounds in both the ground-water and on the surface of aquifer materials, (2) investigate new instrumentation to analyze selected organic compounds in complex matrices, and (3) develop chemical criteria for assessing the environmental impact of hazardous organic compounds on ground-water quality.

APPROACH: Techniques such as solvent extractions, preconcentrations, and resin adsorption will be used to separate organic compounds from water and aquifer materials. Chemical characterization of organic compounds will be made by low and high resolution mass spectrometry, ancilliary techniques such as infrared and High-Pressure Liquid Chromatography (HPLC), with both ultraviolet and fluorescence detectors will be used. Microbiological degradaton, and metabolic pathways of selected pollutants will be studied at one or two field sites.

REPORTS PUBLISHED:

Pereira, W. E., Rostad, C. E., Taylor, H. E., Klein, J. M., 1982, Characterization of organic contaminants in environmental samples associated with Mount St. Helens, 1980 volcanic eruption: Environmental Science Technology, v. 16, p. 387-396.

McKnight, D. M., Pereira, E. W., Ceazan, M. L., Wissmar, R. C., 1982, Characterization of dissoved organic material in surface waters within the blast zone of Mount St. Helens, Washington: Organic Geochemistry, v. 4, p. 85-92.

McKnight, D. M., Pereira, E. W., Rostad, C. E., Stiles, E. A., 1983, Effect of retorted-oil shale leachate on a blue-green alga (anabaena flos-aquae): Bull. Environ. Contam. Toxicol., v. 30, p. 6-16.

Pereira, W. E., Rostad, C. E., 1983, Chemical characterization of organic compounds in leachates from surface-retorted oil shale generated by gas combustion and indirect pyrolysis: Inter. Jour. of Environ. Anal. Chem., v. 15, p. 73-88.

Pereira, W. E., Rostad, C. E., 1983, Terpenoid marker compounds derived from biogenic precursors in Mount St. Helens volcanic ash: Geochim. Cosmochim. Acta., v. 47, no. 12, p. 2287-2291.

Pereira, W. E., Rostad, C. E., Garbarino, J. R., Hult, M. F., 1983, Ground-water contamination by organic bases derived from coal-tar wastes: Environ. Toxicol. and Chem., v. 2, p. 283-294.

TITLE: Organic Geochemistry of Polluted Ground and Soil Waters.

PROJECT CHIEF: Thurman, E. Mike

PROBLEM: Hazardous wastes, both liquid and solid, can contaminate ground water and soil water. These wastes decompose chemically and biologically. The result is a different waste product that is chemically stable and may be mobile in ground and soil waters. The waste product is a high molecular weight organic substance, a product of anaerobic decomposition. These polymeric substances contain pollutants within their structure, carry or complex simple organic compounds and trace metals, and may be toxic in themselves. Because they do not extract into organic solvents, they cannot be analyzed by conventional methods, such as gas chromatography, and little is known of their structure, chemistry, and toxicity. Yet, they make up 50 percent of organic wastes from solid waste disposal and, perhaps, 25 percent of organic wastes from liquid-waste disposal.

OBJECTIVE: (1) Compare the structure and reactivity of polymeric substances in contaminated ground water with that of naturally occurring organic substances and determine their biologic toxicity, and (2) understand the role of polymeric substances in transport of simple pollutants through ground and soil waters.

APPROACH: High molecular weight organic wastes will be characterized by conventional methods including elemental analysis, molecular weight, and functional group analysis. The toxicity of the polymeric substances will be determined by Ames testing and compared with natural polymeric material. The ability of the polymeric organic matter to complex simple pollutants and trace metals will be measured.

REPORTS PUBLISHED:

Thurman, E. M., Wershaw, R. L., Malcolm, R. L., and Pinckney, D. J., 1982, Molecular Size of Aquatic Humic Substances: Organic Geochemistry, v. 4, p. 27-35.

Oliver, B. G. and Thurman, E. M., 1983, The influence of aquatic humic substance properties on trihalomethane potential, in Water chlorination environmental impact and health effects, v. 4, Book 1, Chapter 16, p. 231-241.

Thurman, E. M., and Malcolm, R. L., 1983, Structural study of humic substances: New approaches and methods, in Aquatic and Terrestrial humic materials, eds. Christman and Gjessing, Ann Arbor Science, p. 1-23.

McKnight, D. M., Feder, G. L., Thurman, E. M., Wershaw, R. L., Westall, J. C., 1983, Complexation of Copper by Aquaitc Humic Substances From Different Environments, Biological Availability of Trace Metals, Wildung, R. E., and Jenne, E. A., (ed.), Elsevier, Amsterdam.

Thurman, E. M., 1983, Multidisciplinary research - and experiment: Environmental Science Technology, v. 17: 511 A.

Caine, N., Thurman, E. M., Furbish, D. J., and T. A. Moses, 1983, Water Quality data from the Green Lakes Valley: Long-term Ecological Research data report, Institute of Arctic and Alpine Research, Univ. of Colorado, 46 p.

Oliver, B. G., Thurman, E. M., and R. L. Malcolm, 1983, The contribution of humic substances to the acidity of colored natural waters, Geochemica et Cosmochimica Act, v. 47, p. 2031-2035.

TITLE: Behavior of Natural Polyelectrolytes in Water

PROJECT CHIEF: Wershaw, Robert L.

PROBLEM: Naturally occurring organic polyelectrolytes are highly reactive materials that are present in practically all natural water systems. They interact with both organic and inorganic pollutants and nutrients, and may influence or control the toxicity, rate of movement, and rate of degradation of the pollutants and nutrients in aquatic environments. It is important to be able to identify and quantify these compounds in surface and ground water and in precipitation. Many organic substances are difficult to ionize in the source of a mass spectrometer due to either thermal instability, involatility, molecular size, or their polar nature. Ionization of these types of compounds can be achieved using the recently developed Fast Atom Bombardment ion source.

OBJECTIVE: (1) Isolate and determine the physical and chemical properties of the most abundant organic polyelectrolytes present in natural waters, (2) describe the mechanisms of interaction of pollutants with natural organic polyelectrolytes, (3) determine the types of chemical compounds that result from the chlorination of natural polyelectrolytes, (4) characterize the effect of organic polyelectrolytes on the chemical speciation of major cations (Na, Ca, K) and trace metals (Cu and Fe) in water, (5) develop nuclear magnetic resonance spectroscopic methods for the characterization of humic materials, (6) develop mass spectrometric methods for the analysis of organic compounds in natural waters, and (7) characterize the interaction of organic pollutants from precipitation with soil systems.

APPROACH: Chemically unique polyelectrolyte fractions will be isolated using column chromatography, electrophoresis, and other techniques. Their physical and chemical properties will be determined using small angle x-ray scattering, ultracentrifugation, and atomic, molecular, and magnetic spectroscopy. Carefully characterized organic polyelectrolyte fractions will be used in experiments designed to describe the sorption and solubilization reactions of pollutants and nutrients with natural organic polyelectrolytes. The behavior of aquatic fulvic acid as an electrolyte will be studied by potentiometric titration. Organic pollutants from natural waters will be isolated and identified.

REPORTS PUBLISHED:

McKnight, D. M., Pereira, W., and Ceazan, M., 1982, Characterization of dissolved organic material in surface waters within the blast zone of Mount St. Helens, Washington: Organic Geochemistry, v. 4, p. 85-92.

McKnight, D. M., Feder, G. L., Thurman, E. M., Wershaw, R. L., Westall, J. C., 1983, Complexation of copper by aquatic humic substances from different environments: Science of the Total Environment, v. 28, p. 65-76.

Ecology

Ecological studies provide the knowledge needed to understand how living organisms produce, alter, and accumulate organic and inorganic substances. Historically, ecological studies focused on surface-water environments. Results from the studies have shown that the biological communities both affect and reflect the inorganic and organic geochemistry of water systems. In recent years, the study of contaminated subsurface environments has shown that microbiological processes can have a significant impact on the organic and inorganic geochemistry of the subsurface as well.

Research projects described in this section include surface- and ground-water studies that have relevence to ground-water contamination issues. The studies will help to:

- Characterize the geochemical partitioning of trace metals.
- Develop methods to evaluate sublethal concentration of toxic substances in aquatic ecosystems.
- Determine biochemical transformations of organic compounds.

TITLE: Fate of Organic Chemicals in Subsurface Environments

PROJECT CHIEF: Ehrlich, Garry G.

PROBLEM: Release of various synthetic organic compounds to the environment can cause soil- and ground-water pollution. A better understanding of the processes which control the persistence and movement of these materials is necessary to aid in the prediction of the fate of pollutants in the subsurface and in the design of effective control and abatement techniques.

OBJECTIVE: (1) Determine the biochemical transformation pathways of selected organic compounds using a combination of field observations and laboratory simulations of environmental conditions, and (2) assess the importance of biochemical processes relative to the physical and chemical processes occurring in the subsurface.

APPROACH: Water, soil, and microbiological samples will be collected at field sites where ground water has become contaminated with organic compounds, and analyzed to determine the biochemical transformations that are occurring. Laboratory simulation studies will be used to describe the controls on these transformations.

REPORTS PUBLISHED:

Ehrlich, Garry G., Goerlitz, Donald F., Bourell, and James H., 1981, A liquid chromatographic procedure for fermentation product analysis in the identification of anaerobic bacteria: Applied and Environmental Biology: v. 42, no. 5, p. 878-885.

Ehrlich, G. G., Goerlitz, D. F., Godsy, E. M., Hult, M. F., 1983, "Degradation of phenolic contaminants in ground water by anaerobic bateria: St. Louis Park, Minnesota: Ground Water, v. 20, no. 6, p 703-710.

Godsy, E. M., Goerlitz, D. F., Ehrlich, G. G., 1983, "Methanogenesis of phenolic compounds by a bacterial consortium from a contaminated aquifer in St. Louis Park, Minnesota: Bulletin of Environmental Contamination Toxicology, v. 30, p. 261-268.

TITLE: Effects of Toxic Substances on Aquatic Communities

PROJECT CHIEF: Leland, Harry V.

PROBLEM: Standard methods for evaluating the effect of sublethal concentrations of toxic substances in aquatic ecosystems are not available. Field and laboratory data on the effects of low concentrations of toxicants on function and structure of aquatic communities are largely lacking.

OBJECTIVE: (1) 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, and (2) evaluate methods of assessing effects of chronic exposures of toxicants on individual species and natural aquatic communities.

APPROACH: Methods will be evaluated for assessing effects of chronic exposures of toxic substances released to the environment as a consequence of fossil fuel extraction and combustion. These include tests of hatchability, embryogenesis, and respiratory response in fishes, specific birth rate and survival of critical life stages of aquatic invertebrates, and population growth rate of algae. Physicochemical factors affecting responses and bioaccumulation of these toxic substances will be determined. Trophic dynamics of simplified aquatic ecosystems (experimental streams) exposed to chronic exposures of trace metals and stable organic compounds of fossil fuel origin will be examined.

The utility of the biological test methods for detecting and monitoring small concentrations of toxicants will be determined and variables influencing responses of natural aquatic communities will be examined.

REPORTS PUBLISHED:

Kuwabara, J. S., 1981 Gametophytic growth by macrocystis pyrifera (Phaeophyta) in response to various iron and zinc concentrations: Journal of Phycology, v. 17, no. 4, p. 417-419.

Kuwabara, J. S., 1982, Micronutrients and kelp culture—evidence for cobalt and manganese deficiency in southern California deep seawater: Science, v. 216, no. 4550, p. 1219-1221.

Kuwabara, J. S., 1981, Toxicity to *Selenastraum capricarbutum* (Chlorophyceae) relative to copper introduction rate: Journal of Phycology, (Supplement), v. 17, p. 6.

Leland, H. V., and Kent, E., 1981, Effects of copper on microfaunal species composition in a Sierra, Nevada, California stream: Verhandlungen der Internationale Vereinigung fur theoretische und angewandte Limnologie, v. 21, no. 2, p. 819-827.

Leland, H. V., 1983, Ultrastructural changes in the hepatocytes of juvenile rainbow trout and mature brown trout exposed to copper or zinc: Environmental Toxicology and Chemistry, v. 2, no. 3, p. 353-368.

TITLE: Availability of Trace Elements from Sediments to Aquatic Organisms

PROJECT CHIEF: Luoma, Samuel N.

PROBLEM: The same biota in different environments may differ widely in their susceptibility or their response to trace elements. These differences may, at least partly, be related to the differences in the availability of metals in sediments. However, little is known about the geochemical and physiological factors which 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 which control the partitioning, (2) study the influence of geochemical partitioning of trace metals in sediments upon metal uptake and metal effects in organisms which contact sediments directly, (3) study physiological characteristics of aquatic organisms which affect metal uptake, (4) improve methodology which uses biota and sediments as indicators of geochemical conditions, (5) develop indices or models for predicting the bioavailability of metals, after their release to the aquatic environment, and (6) develop methods for assessing the presence of biological effects from toxic wastes in aquatic communities in nature.

APPROACH: Organisms and sediments will be collected from rivers, lakes, or estuaries, across spatial or temporal gradients of physiochemical conditions. The geochemical partitioning of trace metals between the solid and liquid phase will be analyzed through the use of chemical extractions and mathematical models. The relationship of metal concentrations in organisms to the specific geochemical gradient under study will be statistically assessed. Laboratory studies will be used to assess the biological influences on metal burdens in animals, such as animal size, intraspecific differences in metal tolerance, and physiological controls on metal uptake and metabolism. Sediments will be modified, or well-defined model sediments will be used in laboratory studies of metal uptake by organisms to identify physiocochemical factors which affect metal availability, and to test models derived from field studies.

REPORTS PUBLISHED:

Luoma, S. N., and Cloern, J. E., 1982, Impact of waste water discharge on biological communities in San Francisco Bay; in Kockleman, W. J., Levinton, H. E., and Conomos, T. J., San Francisco Bay: Use and Protection: AAS-Pac. Division, San Francisco, p. 137-161.

Luoma, S. N., and Bryan, G. W., 1982, Statistical study of environmental factors controlling concentrations of heavy metals in burrowing bivalve Scrobicularia Plana and Polychaete Nereis Diversicolor: Estuarine Coastal Shelf Science., v. 15, no. 1, p. 95-108.

Inorganic Geochemistry

The movement of organic and inorganic solutes through the subsurface may be affected by a variety of reversible or irreversible chemical reactions such as ion exchange, mineral solution or precipitation, ion filtration, adsorption/desorption, oxidation/reduction, and complexation. Inorganic reactions with aquifer materials can change the aquifer's hydraulic characteristic as well as its surface chemistry. The research projects described in this section will contribute to the understanding of:

- Methods to characterize the chemical composition of sediment surfaces.
- Clay-water reactions, particularly with regard to the interaction of clay minerals with waste fluids.
- Adsorption behavior of trace organic and inorganic solutes on particulate materials such as aluminosilicate minerals and colloids, and solids of biogenic origin in natural systems.
- The theory of ion-exchange based on the crystal structure of clay.
- The relationship of chemical quality of natural water and human health.
- The effects of saline environments on chemical reactions.
- The factors that control redox potential in natural systems.
- The relationship between ground-water quality and human health.

TITLE: Spatial Distribution of Chemical Constituents in Ground Water

PROJECT CHIEF: Back, William

PROBLEM: Reactions and processes that control the chemical character of ground water in regional limestone aquifers need to be identified in order to predict physical and chemical changes that occur in both natural and stressed environments.

OBJECTIVE: Study geochemical reactions that relate to: (1) karstification and other geomorphic processes, (2) generation, migration, and attenuation of leachate components, (3) processes of isotopic fractionation, and (4) diagenesis of organic constituents in sediments.

APPROACH: Areas are selected to demonstrate the occurrence, extent, rate, and consequences of chemical reactions. Changes in porosity and permeability by karstification will be studied. Degradation and migration of organic compounds and isotopic fractionation will be investigated at landfills, in lake sediments, and in sulfide-rich ground water. Comparative studies of regional ground-water systems will be undertaken to evaluate the environmental and geochemical consequences of hydrogeologic processes occurring in limestone terranes.

REPORTS PUBLISHED:

Back, William, and Letolle, Rene, 1981, eds., Symposium on geochemistry of ground water: in Developments in Water Science: Elsevier, v. 16, 369 p.

Bredehoeft, J. D., Back, William, and Hanshaw, B. B., 1982, Regional concepts in the United States: Historical perspectives; in Geol. Soc. of America Special Paper 189, p. 297-316.

Rye, R. O., Back, William, Hanshaw, B. B., Rightmire, C. T., and Pearson, F. J., Jr., 1981, The origin and isotopic composition of dissolved sulfide in ground water from carbonate aquifers in Florida and Texas: Geochem. Cosmochima Acta, v. 45, p. 1941-1950.

TITLE: Characterization of Selected Clay-Mineral Assemblages and Their Interaction With Pore Fluids

PROJECT CHIEF: Bodine, Marc W., Jr.

PROBLEM: Clay minerals commonly are the dominant constituents in soils, sediments, and sedimentary rocks. Clays also are among the most chemically complex of sedimentary minerals and are very sensitive to changes in the chemical (fluid) environment. Interaction between migrating fluids and clay minerals results in both modification of the host pore-fluid chemistry and in modification (and concomitant change of physical and chemical properties) of the clay-mineral assemblage. Effects on clays include: absorption or exchange (organic molecules/inorganic ions) in expandable clays (smectites and vermiculites) resulting in significant chemical modification, but with little or no modification of the clay structure; transformation, or, in some cases, destruction of the fundamental clay structure; and neoformation of clays through dissolution of nonclay constituents and precipitation of solutes as clays. Characterization of clays, their interaction with fluids (particularly waste fluids) and rates of their reactivity are required to evaluate and predict behavior of waste disposal and containment, and to assess the effects of migration (planned or leakage) through clay-bearing strata.

OBJECTIVE: (1) Characterize clay-mineral assemblages in selected sedimentary facies (perhaps with knowledge of pore-fluid compositions) using field observations and sample collection followed by laboratory measurements of crystallographic properties and chemical composition, (2) assess the role of fluid interaction in the genesis of the assemblages through observational, thermochemical, and experimental methods; and (3) where possible, collect and characterize clay-mineral assemblages within and adjacent to areas of contact with waste fluids and assess the effects of fluid interaction.

APPROACH: Present activities include: (1) continuation of acquisition of laboratory equipment and facilities for conducting comprehensive clay mineral research and associated analysis-experimentation; (2) characterization of clay-mineral assemblages, and assessment of their genesis and role of fluid interaction from a drill core in the Paradox Basin (Utah) in strata whose depositional facies range from fluvial (continental) through near-shore tidal and deltaic (mixed) into normal marine and marine salts (hypersaline with Ca-rich residual brines); (3) study of clay geochemistry in a uranium-vanadium-rich environment (that is, around uranium deposits) to assess the extent to which heavy metals are incorporated into clay structures in natural environments and to determine the relevant processes; (4) study of the general clay formation/transformation processes in natural porous media which might accompany the uptake or release of various ionic species over long periods of time; and (5) planning for experimental investigation of the mechanisms by which trace metals are incorporated into the clay structure.

TITLE: Partitioning of Solutes between Solid and Aqueous Phases

PROJECT CHIEF: Davis, James A., III

PROBLEM: When solutes are introduced into a ground-water system, such as by artificial recharge, or into surface waters, such as by surface runoff, reactions may occur between the dissolved solutes and native solid materials. Detailed knowledge of the chemical reactions which occur at solid surfaces is required to understand and predict the distribution of trace metals between solid and aqueous phases.

OBJECTIVE: (1) Study, from a theoretical perspective and including electrical double layer theory, the adsorption behavior of inorganic and organic solutes on particulate materials which are important in natural systems, including aluminosilicate minerals, 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 (3) develop a data base of surface stability constants which is compatible with existing computer models of chemical equilibrium and which could be used in the field evaluation of solute transport models.

APPROACH: Laboratory experiments will be conducted using physical-chemical techniques to characterize surfaces and to measure adsorption behavior for a variety of solutes, surfaces, and water compositions. Kinetic and equilibrium studies will be made with controlled laboratory solutions to evaluate the importance of surface reactions for a given solute in a given geochemical environment. Quantitative phenomenological models will be developed to describe observed results and predict the behavior of solutes under other experimental conditions with the aid of a computer. Field studies will be conducted periodically to assess the applicability of the models to natural aqueous systems.

REPORTS PUBLISHED:

Berelson, W., Hammond, D. E., and Fuller, C., 1982, The use of radon-222 as a tracer for vertical mixing and benthic fluxes in the southern California borderlands: Earth and Planetary Science Letters, v. 67, no. 1, p. 41-54.

Davis, J. A., 1982, Adsorption of natural dissolved organic matter at the oxide/water interface: Geochimica Cosmochimica Acta, v. 46, no. 11, p. 2381-2393.

Davis, J. A., and Gloor, R., 1981, Adsorption of dissolved organics in lakewater by aluminum oxide: Environ. Sci. Tech., v. 15, no. 10, p. 1223-1229.

Fuller, C., Davis, J. A., Ball, N. B., and Leckie, J. O., 1983, Trace element adsorption onto calcareousaquifer materials: Abstract, 6th International Symposium on Environmental Biogeochemistry, p. 59-60.

Fuller, C., and Hammond, D. E., 1983, The fallout rate of Pb-210 on the West Coast of the United States: Geophysical Research Letters, v. 10., no. 12, p. 1164.

Fuller, C., and Hammond, D. E., 1982, Sediment accumulation in San Francisco Bay, determined by Pb-210 balances: EOS, v. 63, no. 45, p. 947.

Hammond, D. E., and Fuller, C., 1982, Sedimentation rates and resuspension of suspended particles in San Francisco Bay, determined by Th-234: EOS, v. 63, no. 45, p. 947.

Leckie, J. O., Ball, N. B., Cederberg, G. A., Davis, J. A., and Fuller, C., 1983, Adsorptive control of cadmium mobility in a groundwater aquifer: experimental and mathematical modeling: Abstract, 6th International Symposium on Environmental Biogeochemistry, p. 58-59.

Luoma, S. N., and Davis, J. A., 1983, Requirements for modeling trace metal partitioning in oxidized estuarine sediments: Marine Chemistry, v. 12, no. 1, p. 159-181.

Simpson, H. J., Trier, R. M., Toggweiler, J. R., Mathieu, G., Deck, B. L., Olsen, C. R., Hammond, D. E., Fuller, C., and Ku, T. L., 1982, Radionuclides in Mono Lake, California: Science, v. 216, no. 1, p. 512-514.

TITLE: Geochemistry of Clay-Water Reactions

PROJECT CHIEF: Eberl, Dennis D.

PROBLEM: Clay minerals may influence the chemistry of ground water and other aqueous solutions through precipitation-, dissolution-, and ion-exchange reactions. An understanding of these reactions is also crucial for understanding the fate of toxic wastes in ground water.

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

APPROACH: Theoretical models will be tested and developed through laboratory experiments that include the measurement of exchange isotherms with well characterized clay minerals. Field work will include the study of clay-water reactions in natural systems.

REPORTS PUBLISHED:

Whitney, G., and Eberl, D. D., 1982, Mineral paragenesis in a talc-water experimental hydrothermal system: American Mineralogist, v. 67, p. 944-949.

Rimmer, S. M., Eberl, D. D., 1982, origin of an underclay as revealed by verticle variations in mineralogy and chemistry: Clays and Clay Minerals, v. 30, no. 6, p. 422-430.

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

PROJECT CHIEF: Feder, Gerry L.

PROBLEM: In recent years, there has been increasing interest and study concerned with the relationships between the chemical quality of natural water and human health and disease. After excluding nonenvironmental factors, it appears that local and regional differences in water quality may have an effect on health and disease.

OBJECTIVE: Determine the relationships between the chemical quality of natural water and human health and disease.

APPROACH: Identify chemical constituents in natural water that are most likely to affect health and cause disease. Determine the temporal and spatial associations between specific chemical characteristics of water and specific states of health and disease. Known high-risk factors related to geographic areas (for example, urban environment, mining activity) will be excluded in order to increase the likelihood of detecting risk factors associated with natural water quality. Initially both the medical and hydrologic aspects of the study will rely on existing data from data storage centers such as the U.S. Geological Survey and the U.S. Bureau of Vital Statistics. Field collection of new data will be planned as necessary.

REPORTS PUBLISHED:

Feder, G. L., 1982, Ground-water chemistry, Fort Union Coal Region, in Ebens, R. J., and others, Geochemistry of some rocks, mine spills, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional paper 1237, p. 21.

Feder, G. L., 1982, Ground-Water chemistry, Poplar River basin, Montana, and Saskatchewan, in Ebens, R. J., and others, Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 24.

Feder, G. L., and Hopps, H. C., 1981, Variations in drinking water quality and the possible effects on human health, in Hesmphill, D. D., ed., Trace substances in environmental health - XV: Columbia, Mo., University of Missouri Press, p. 96-103.

Feder, G. L., and Krothe, N. C., 1981, Results of a reconnaissance water-quality sampling program of the Ogallala Aquifer in Colorado, Kansas, Nebraska, Oklahoma, South Dakota, and Texas: U.S. Geological Survey Water-Resources Investigations 81-65, 7 p.

Feder, G. L., 1982, Ground-water chemistry, Powder River coal region, Montana and Wyoming, in Ebens, R. J., et al., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 24.

Hopps, H. C., and Feder, G. L., 1982, The geochemical environment, an important Factor in Prospective Medicine, in Lindberg, D. A. B., Collen, M. F., and Van Brunt, E. E., eds., First AMIA Congress on Medical Informatics, San Francisco, Calif., May 2-5, 1982, Proceedings: New York, Masson Publishing, p. 381-382.

McKnight, D. M., Feder, G. L., and Stiles, E. A., 1981, Effects on a blue-green alga of leachates of ash from the May 18 eruption, in Lipman, P. W., and Mullineaux, D. R., eds., The 1980 Eruptions of Mount St. Helens, Washington: U.S. Geological Survey Professional Paper 1250, p. 733-741.

McKnight, D. M., Feder, G. L., and Stiles, E. A., 1981, Toxicity of Mount St. Helens ash leachate to a blue-green alga: U.S. Geological Survey Circular 850-F, 14 p.

McNeal, J. M., and Feder, G. L., 1982, Stream-sediment chemistry of the Uinta and Piceance Creek Basins, Utah and Colorado, in Ebens, R. J., and others, Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 24.

TITLE: Water Chemistry of Sediment Surface Coatings

PROJECT CHIEF: Goldberg, Marvin C.

PROBLEM: The chemical composition of natural water can be influenced by sediment surface reactions. This is attributed to sorption on the sediment surface of trace metals, pesticides, and salts. These sorbed species are interactive across the solid-liquid interface and may move in either direction in response to changes in chemical potential set up on either side of the interface. To understand the processes controlling a main source of materials that enter into and exist in water systems, it is necessary to understand the variety of reactions taking place between the solid and liquid phases. Knowledge of the processes by which sediment acquires coatings, the chemical composition of the coating, and the chemical reactivity of the coatings when exposed to various bulk water compositions, is necessary to predict, and, perhaps, manipulate water quality.

OBJECTIVE: (1) Study rate-determining sorption processes that occur on a variety of surfaces of naturally occurring sediments and correlate these sorption reactions with specific molecular species that reside on the surface; and (2) examine the chemical processes by which sediment coatings are formed and the nature of the bonding between coatings and sediment surfaces.

APPROACH: Spectroscopic methods, mainly Fourier transform infrared spectoscopy, Laser Raman spectroscopy, and 3-dimensional fluorescence spectroscopy, will be used to determine the surface chemical composition of natural and prepared sediment coatings. Supplemental information on the surface composition will be obtained by Auger and Low Electron Excitation spectroscopy. The sorption reaction of Ca, Co, Ni, Cu, Fe, phosphate, sulfate, and silicate on gibbsite-and/or goethite-type coatings will be used to study surface bonding mechanism between the coating and the sorbing material, the surface chemical reactivity to these species, and the speciation of each sorbed component. Characterization of fluorescence organic surface coatings and micelles in water will be done on natural water samples to evaluate the sorption influence of these materials on the local water composition.

REPORTS PUBLISHED:

Goldberg, M. C., 1982, A method for calculating the pesticide partition between sediment and water for environmental systems: The Science of the Total Environment, v. 24, p. 73-84.

Goldberg, M. C., and Weiner, E. R., 1982, The use of Fourier transform infrared spectroscopy to characterize sediment coatings of phosphate on the substrates goethite and pyrolucite: 24th Rocky Mtn. Conference, Aug. 1-5, 1982, Denver, CO.

Weiner, E. R. and Goldberg, M. C., 1982, Optimizing the selectivity of standard spectrophotoflurometers with computer control: American Laboratory, v. 14, no. 9, p. 91-103.

Cunningham, K. M., and Goldberg, M. C., 1983, The aqueous photolysis of ethylene glycol adsorbed onto goethite: Proceedings of the 185th National Meeting of the American Geochemical Society, Environmental Division, March 20-25, 1983, Seattle, Washington, p. 215-216.

Goldberg, Marvin C., 1983, Fluorescence spectroscopy applied to the interpretation of fulvic acid bonding to Cu=2 in aqueous systems: 25th Rocky Mountain Conference, August 15-19, Denver, Colorado.

Goldberg, M. C. and Cunningham, K. M., 1983, The photolysis of goethite and organic materials in aquatic environments: Proceedings of the 185th National Meeting of the American Chemical Society, Environmental Division, March 20-25, Seattle, Washington, p. 213-214.

Goldberg, Marvin C. and Cunningham, Kirkwood, M., 1982, Calculation of the dissociation constants for a humic acid sample based on the presence of isobestic points in the fluorescence spectrum: 24th Rocky Mountain Conference, Denver, Colorado, August 1-5.

Goldberg, Marvin C. and Weiner, Eugene R., 1982, The use of fourier transform infrared spectroscopy to charterize sediment coatings of phosphate on the substrates geothite and pyrolusite: 24th Rocky Mountain Conference, Denver, Colorado, August 1-5.

TITLE: Methods Development for the Determination of Inorganic Partitioning in Sediments

PROJECT CHIEF: Horowitz, Arthur J.

PROBLEM: There is a strong association of numerous inorganic elements and compounds with both suspended and bottom sediments and aquifer materials. Lacking are the procedures to investigate and delineate the physical and chemical partitioning of inorganics with the surfaces of these materials.

OBJECTIVES: (1) Develop acceptable "production-line" methods for the total trace metal analysis of sediments; (2) develop a size separation technique which does not alter chemistry; and (3) investigate and evaluate methods for determining trace metal-sediment partitioning.

APPROACH: Methods for each objective will be examined for applicability to various types of sediment, reproducibility, ease of use with emphasis on adaptability to automation and utility in the U.S. Geological Survey's central laboratory system, and maximum data recovery for minimal effort. Work will concentrate on a small suite of diverse samples to maximize comparisons and to determine method utility.

TITLE: Mineral-Water Interaction in Saline Environments

PROJECT CHIEF: Jones, Blair F.

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

OBJECTIVE: Utilize saline environments to determine mechanisms and relative importance of mineralogic processes which influence the solute composition of natural water.

APPROACH: Field study and laboratory analysis will be made of saline waters and associated deposits, mostly from surficial sites or shallow cores in selected pilot or problem areas. Solid and solution phase separation and examination involves high speed gradient and gradient centrifugation, microscopy, x-ray diffractometry, and special potentiometric apparatus, as well as detailed constituent analysis of both solids and solutions. Composition of these materials will be related to the hydrochemical environment, thermodynamic conditions and structural elements of associated mineral species.

REPORTS PUBLISHED:

Eberl, Dennis D., Jones, Blair F., and Khoury, Hani N., 1982, Mixed-layer Kerolite/Stevensite from the Amargosa Desert, Nevada: Clays and Clay Minerals, v. 30, no. 5, p. 231-326.

Khoury, Hani N., Eberl, Dennis D., and Jones, Blair F., 1982, Origin of magnesium clays from the Amargosa Desert, Nevada: Clays and Clay Minerals, v. 30, no. 5, p. 327-336.

TITLE: Redox Reactions in Ground Waters

PROJECT CHIEF: Thorstenson, Donald C.

PROBLEM: Oxidation-reduction (redox) potential remains the least understood major control on natural water chemistry. An understanding of the processes governing redox reactions is necessary to understand the ground-water geochemistry of compounds of multivalent elements such as iron, manganese, or uranium and other actinides.

OBJECTIVE: (1) Identify controls on redox potential in specific natural systems; (2) evaluate processes responsible for the distribution of oxygen and carbon dioxide in the unsaturated zone; (3) use computer models of specific redox problems in ground-water systems; and (4) measure gas compositions and tritium distribution in the unsaturated zone at waste disposal sites.

APPROACH: Fundamental thermodynamics of redox processes will be used to study natural-water geochemistry. Gas composition and isotopic characteristics of carbon dioxide will be used in the deep unsaturated zone. Computer models will be used to study specific redox problems in ground-water systems.

PROBLEM-ORIENTED RESEARCH—FIELD STUDIES

To evaluate how well the current state-of-knowledge of earth-sciences processes can quantitatively describe real-world problems, sites were selected to study ground-water contamination resulting from a crude oil pipeline break near Bemidji, Minnesota; the infiltration of creosote and pentachlorophenol from waste disposal pits at Pensacola, Florida; and the infiltration of sewage treatment effluent on Cape Cod, Massachusetts.

To select the sites a list of pertinent earth-science, safety, legal, and logistical criteria were developed. An acceptable site would be one that is relatively simple in terms of hydrogeologic setting, has a definable contaminant source and record of disposal, provides a relatively safe working environment, is not in litigation or subject to immediate remedial action, and is accessible. Project descriptions for candidate sites were requested from WRD scientists. Fourteen of the candidate sites were chosen for more intensive review from which the three were selected.

The contaminants at the three sites are responsible for many ground-water contamination problems throughout the Nation. Thus, although the field studies are intended to improve scientific capability rather than solve the specific problems at the sites, the knowledge gained through these studies should have transfer value to other sites where similar contamination has occurred.

Although predominantly ground-water studies, all three sites include studies of the unsaturated zone and surface water. Because ground-water contamination generally occurs in shallow systems, the unsaturated zone and surface-water systems often become impacted by contaminants in ground water. Inclusion of surface water and unsaturated studies is necessary as a "sink term." Loss of organic constituents to the unsaturated zone through such processes as volatilization or by entrapment in interstitial pore space, or to the surface water through ground-water discharge, must be understood in order to understand the "fate" of these constituents in ground water.

The site studies are being conducted by scientists within District offices in the three States, the National Research Program of the U.S. Geological Survey, and by scientists on the research staffs of several universities.

Infiltration of Sewage-Plant Effluenty

Cape Cod, Massachusetts

Background

Otis Air National Guard Base is located in the western side of Cape Cod and is situated on a glacial outwash plain that is underlain by an unconfined aquifer. Since 1938, the Base's sewage-treatment plant has treated over 8 billion gallons of sewage, which enters the aquifer through infiltration beds. As a result of this long-term discharge, a plume of sewage formed in the sand and gravel aquifer that is currently 2,500 to 3,500 feet wide, 75 feet thick, and more than 11,000 feet long.

The sand and gravel aquifer is 90 to 140 feet thick and is underlain by silty sand and till. Recharge from precipitation, estimated to be 21 inches per year, has depressed the plume 20 to 50 feet below the water table. Ground water flows laterally through the sand and gravel at a rate of 0.7-1.5 feet per day.

Problem

Better methods are needed to measure the spatial variation of hydraulic conductivity and dispersivity. Hydraulic conductivity can be measured by a variety of well-known techniques, but the results generally are average values for a volume of the aquifer. Small-scale variation in hydraulic conductivity, not accounted for in the spatially averaged values, significantly may affect the rate of contaminant movement.

Dispersivity generally is measured in the field by tracer tests or by simulation of plumes with mathematical models. Values for dispersivity obtained from field tests generally are dependent on the scale of measurement. Dispersivities obtained from column experiments are in the order of centimeters, but dispersivities obtained using field data for existing plumes are on the order of tens of meters. The apparent discrepancy is due in part to the spatial averaging of the field measurements and to the numerical analysis. In a sense, the fitted dispersivity in the field-scale problem may not represent a real physical parameter, but may be a "catch-all" to account for the simplification of aquifer heterogeneity and contaminant distribution in the numerical method. The paradox of using a fitted dispersivity in a predictive model is that an existing plume is required in order to determine the dispersivity used in the model. In cases where a plume has not yet developed, it is common practice to use fitted dispersivities from sites in similar geohydrologic settings.

Information on trace metals, nutrients and organic solutes, and mineralogical composition of the aquifer are a necessary part of the research on solute transport, but little detailed information is available. These data will delineate the extent of the plume and also will be used in chemical modeling of the plume.

Little is known about bacterial populations in the sewage plume and the nature and extent of organic and inorganic processes they mediate. Detailed knowledge of these microbiologically mediated processes is necessary in order to explain the fate of many organic and inorganic constituents in the plume.

Objective

The objectives of the study are: (1) to develop a better understanding of spatial variation of hydraulic conductivity and dispersivity for the prediction of contaminant movement in the field, and (2) to better understand the geochemical and microbiological processes that affect the fate of the contaminant in the subsurface.

Approach

The following hypotheses are proposed for testing as part of the interdisciplinary study.

Hydrogeology

Hypothesis 1.—Transport of solutes in ground water is sensitive to 3-dimensional geologic and hydrologic characteristics of aquifers, even in sand and gravel in which flow is mostly horizontal. The effect of heterogeneity and 3-dimensional flow on transport will be studied by simulating the sewage plume using a numerical model. The model will be calibrated to simulate movement of solute in the plume from 1978 to the end of the study, monitored by collecting water samples periodically from wells over a 4 to 6 year period. The existing network of 60 wells will be supplemented by drilling new wells where the plume is poorly defined and where large concentration changes are expected with time. The new wells also will be used to improve description of the geohydrology and flow system, especially near the infiltration beds and kettle-hole ponds.

The calibrated model will be used to determine which aquifer characteristics affect transport most, allowing us to show where field efforts should be directed in collecting data for predictive models. The modeling results will be compared to earlier 2-dimensional models to show how spatial averaging of properties, especially dispersivity, affects the results of the simulation. Incorporation of chemical reactions in the model will be attempted.

Hypothesis 2.—Advective and dispersive transport can be predicted by stochastic analysis of the spatial distribution of hydraulic conductivity and porosity.

A tracer test will be coupled with a detailed description of hydrogeologic variability to test a stochastic approach for predicting solute transport. Several potential tracer-test sites, where flow is uniform and traceable have been identified for at least 1,000 feet. The variability of hydraulic conductivity and porosity in the projected path of the tracer plume will be determined as described above and will be quantified using statistical techniques. From the stochastic description of hydraulic conductivity and porosity, the dispersivity tensor will be predicted, and a stochastic model will be used to simulate movement of the tracer plume.

A tracer test, in which a finite-duration pulse of a conservative tracer is injected into the aquifer, will be used to test the theoretical predictions. The tracer will move with the natural flow and will be tracked for 4-5 years until it has moved about 1,000 feet. Techniques to monitor the tracer plume in three dimensions but do not cause apparent dispersion due to sampling procedures will be developed.

The observed and predicted tracer plumes will be compared to evaluate the theoretical relationship between heterogeneity and transport. The stochastic approach may be applied to the sewage plume to test applicability of the method to field-scale plumes.

Geochemistry

Hypothesis 1.—Hydrophobic sorption is a major process in chemical transport.

Three mechanisms of adsorption will be examined: hydrophobic effect, hydrogen bonding, and ion exchange. The hydrophobic effect will be measured on neutral solutes of low solubility and on detergents with surfactant qualities. Hydrogen bonding of acids on sand and silt will be studied, as well as the ion exchange of ammonia, amino acids, and trace metals on aquifer solids. Distribution coefficients and adsorption isotherms will be determined, and column experiments and field experiments are planned.

Hypothesis 2.—Detergents and polymeric acids lower adsorption of organic compounds and cause them to be transported by ground water.

The decrease in sorption of organic compounds by surfactants and detergents will be studied, both in the laboratory and in the field. An example compound is coprastanol, a fecal steriod that has a large octonal/water partition coefficient and sorbs onto the aquifer by the hydrophobic effect. The change in sorption caused by detergents, and their ability to increase the transport organic solutes that otherwise would be tightly retained by the aquifer, will be measured.

Hypothesis 3.—Detergents and polymeric acids increase the transport of trace metals that might otherwise be retained by the aquifer.

The organic-metal interaction will be studied. Detergents and polymeric acids will be isolated and their binding constants with important metal ions present in the plume, such as iron, manganese, copper, and cadmium will be determined.

Microbiology

Hypothesis 1.—A majority of the ground-water bacterial and microbial activity in the contaminated zone takes place at solid surfaces.

The nature of the indigenous microbial community within an uncontaminated zone will be compared with microbial communities within selected zones of the plume. Comparisons will be based on total biomass, fractions of the total population that are metabolically active, and representative estimates of heterotrophic and autotrophic activities. The results of these studies will determine the types of aquifer samples necessary for subsequent investigations of microbial activities.

Hypothesis 2.—Several chemically distinct zones exist within the plume, caused by the predominant terminal electron-accepting processes of distinct groups of bacteria.

Processes of microbial degradation will be studied from two perspectives. First, the zones of the predominant terminal electron processes (O_2, NO_3, SO_4, and CO_2 reduction) will be delineated. Attempts will be made to measure the actual rates of each process. This will allow estimation of the amount of organic carbon mineralized within each zone and the rates of transformation of inorganic solutes. Second, the turnover of organic acids of low molecular weight and amino acids will be measured to examine the effect of microbial activities upon organic solute transport.

Hypothesis 3.--The presence and metabolic activities of adherent bacteria significantly affect the movement and ultimate fate of manganese and possibly of other heavy metals within the uncontaminated zone.

The effect of bacterial populations upon the transport of heavy metals within the contaminated zone will be studied. Initial emphasis will be placed upon delineation of potential bacterial roles in the movement and fate of manganese, because it is likely that the behavior of this metal within the plume may be strongly influenced by microbial activities. The effect of adherent bacteria upon adsorption of cadmium, copper, and manganese to solid aquifer material will be investigated in the laboratory, using core material obtained from selected zones of the plume.

Petroleum Pipeline Break

near Bemidji, Minnesota

Background

The study site is at a major pipeline break (10,000 barrels) of crude petroleum that occurred near Bemidji, Minnesota, on August 20, 1979. Clean-up efforts recovered 6,434 barrels and some of the oil was burned off. Regulatory and remedial action has been completed. Oil percolated through the unsaturated zone and at present (1983) there is as much as four feet of oil floating on the water table. Ground water contaminated by the oil moves through the glacial outwash aquifer towards a shallow lake.

Problem

A large proportion of ground-water contamination results from the discharge of toxic organic liquids. Organic substances from the liquids can move through the subsurface as vapors, dissolved constituents of water, a separate fluid phase, or as aggregates of individual compounds that are neither truly dissolved nor a distinct fluid phase. A substantially improved understanding of the physical, chemical, and biologic processes controlling the dissolution and movement of organic liquids is needed in order to better predict contaminant behavior.

Objective

The objectives of the project are to obtain a more complete understanding of the mobilization, transport, and fate of petroleum derivatives in ground water and to use this understanding to develop predictive models of contaminant behavior in the subsurface.

Approach

The following hypotheses are proposed for testing as part of the interdisciplinary research study.

Hydrogeology

Hypothesis 1.—A comprehensive mathematical model can be developed to simulate ground-water contamination resulting from the discharge of crude oil.

The literature on petroleum migration in the subsurface will be reviewed for applicability to near-surface pressures and temperatures and to the selected field problem. The types of processes included in the model to be developed will depend upon the requirements of the site, but it is anticipated that the major processes will include:

1. periodic inputs from the unsaturated zone owing to percolating precipitation,
2. development, movement, and ultimate stabilization of a petroleum lens floating on the water table,
3. changes in the distribution of petroleum between the saturated and unsaturated zone owing to water-table fluctuations,
4. loss of petroleum through the unsaturated zone by volatilization, and
5. preferential dissolution and other modes of entrainment of the petroleum, leading to changes in the physical and chemical properties of the fluid source.

In addition to these aspects which deal primarily with influence of the fluid source, the model will address sorption and biologic processes to the extent that these reactions can be determined and expressed mathematically.

Hypothesis 2.—Laboratory-scale investigations can be used to simulate major phenomena that affect multiphase movement of petroleum products in the subsurface.

Column models will be used to estimate bulk transfer of petroleum from the unsaturated zone using different characteristic porous media, initial residual saturations, and flushing rates and timing. Plate models may be useful in visually and quantitatively assessing the effect of fluctuating water-table levels on the distribution of petroleum floating on the water table and in the unsaturated zone.

Geochemistry

Hypothesis 1.—Petroleum products can be transported as non-ideal solutes such as micelles, globules, and humic-bound substances.

The literature on petroleum migration, colloid chemistry, and natural polyelectrolytes will be surveyed to identify mechanisms that may be operating in the fields at prevailing temperatures, pressures, and concentration of contaminants, humic and fulvic substances, and other natural surfactants.

The likelihood of substantial transport of non-ideal solutes such as micelles, globules, and humic-bound substances will be broadly assessed through (1) field and laboratory measurements of oil-water-sediment partioning, (2) comparison of compound concentration in the aqueous phase with octanol-water partition coefficients, and aqueous solubilities, and (3) visual inspection of water and sediment samples for surface films.

Hypothesis 2.—Differential dissolution, volatization, and sorption processes may result in fractionation of the original source.

Characteristics of the oil, water, sediment, and gas phases will be defined by: (1) bulk properties (primarily physical characteristics used in the petroleum industry), (2) classes of compounds (alkanes, alkenes, light aronmatics, polynuclear aromatics, NSO heterocycles, and asphaltenes), and major individual compounds.

Initial samples of oil, water, sediment, and gas will be collected at critical locations including: the volume at which oil is in contact with water, at the water table, and cores and wells within the plume in the unsaturated zone.

Comparison may be made of the measured distribution between phases of selected compounds with partition coefficients, calculated from column experiments. Retardation factors observed in column experiments will be compared with apparent retardation in the field.

Hypothesis 3.—Organic components in petroleum may affect the natural organic material in sediment and may selectively degrade to other compounds and/or sorb on the solid phases.

Water and sediment will be analyzed for organic carbon in the area of the petroleum spill. The soil, aquifer material, and lake sediment will be analyzed for selected organic compounds and these results compared to the constituents found in petroleum. The C^{12}/C^{13} ratios of organic and inorganic carbon in selected samples will be measured to determine if the isotopic signal of the petroleum is altered by degradation and if it varies significantly from that of autochthonous organic material. The movement of petroleum along the flow path will be studied to identify the reactions that affect the concentrations of individual compounds in water and sediment. After the initial phase of the work is completed, additional studies will be undertaken to further delineate the reaction pathway in the unsaturated and saturated zone.

Microbiology

Hypothesis.—Microbiologic activity in the subsurface can degrade many consitutents of petroleum under prevailing conditions.

The first phase of microbiological studies will consist of enumeration of physiological types on aquifer solids obtained from core samples and in water samples from contaminated and uncontaminated zones. A bioassay procedure to enumerate hydrocarbon-degrading bacteria in contaminated and uncontaminated areas also will be tested.

Infiltration of Creosote and Pentachlorophenol, Pensacola, Florida

Background

American Creosote Works Incorporated (ACW) is located in northwest Florida, within the city limits of Pensacola. The 18-acre plant site is situated approximately 600 yards north of Pensacola Bay near the entrance to Bayou Chico. The plant was operated from 1902 until December 1981. During the 80 years of continuous operation, wastewaters generated from the use of creosote and pentachlorophenol (PCP) in the wood-treatment process were discharged into two unlined surface impoundments which are in direct contact with the sand-and-gravel aquifer, the principal source of water in northwest Florida. Data collected from the hazardous-waste site indicate that the areal extent of ground-water contamination is confined to approximately 26 acres downgradient from the source. The approximate vertical extent of contamination of the aquifer extends to 90 feet at its greatest depth, just downgradient from the ponds.

Problem

Despite the 80 years the plant had been in continuous operation (1902-1981), ground-water contamination has remained confined to a much smaller portion of the aquifer than might normally occur for conservative (nonreactive) contaminants. Laboratory and field studies at the Pensacola site indicate that methanogenic fermentation of selected phenolic compounds may significantly contribute to attenuation of concentrations of phenolic compounds in ground water, but other processes related to hydrogeologic factors and geochemical properties of the aquifer material may also contribute to the attenuation of the contaminants.

Objective

The objective of the research at the Pensacola site is to quantitatively and qualitatively define the biological, physical, and chemical processes that occur in ground and surface waters that have been contaminated with creosote and PCP, and the extent to which they contribute to attenuation of contaminants in various hydrologic systems.

Approach

The basic experimental design of the research program at Pensacola divides the hydrologic system into four components: (1) unsaturated zone, (2) saturated zone, (3) stream system, and (4) marine system. Physical, chemical, and biological characteristics of the water in each hydrologic component will be measured in the field. Concurrently, laboratory studies will be conducted to determine rate dependencies of selected chemical and microbial processes. Mathematical models will be used to simulate physical, chemical, and biological processes affecting the transport of selected organic and inorganic constituent in the hydrologic system.

The following research hypotheses are proposed for testing at the Pensacola site:

Hydrogeology

Hypothesis.—Hydrologic factors at ACW significantly contribute to the attenuation of organic and inorganic constituents in ground water at ACW.

A ground-water monitoring network will be used to define vertical and horizontal hydraulic gradients near ACW, and to determine the quality of water in the aquifer. Lithologic samples will be obtained and analyzed for grain size, porosity, bulk mineralogy (x-ray diffraction), specific yield, and chemistry (x-ray fluorescence).

A quasi 3-dimensional regional ground-water flow model will be evaluated with regard to its application to the sand-and-gravel aquifer near ACW. Modifications as appropriate will be made to utilize the model to develop a detailed interpretation of the hydrologic flow system in the upper portion of the sand-and-gravel aquifer near ACW.

Using inorganic and organic chemical data, changes in concentrations due to sorption, and microbial information (described later), a solute transport model will be developed to separate physical, chemical, and microbial processes in the transport of contaminants at ACW and their relative importance in the attenuation process.

Geochemistry

Hypothesis 1.—Geochemical processes that affect the concentration of inorganic chemicals in ground water include: generation of gases, ion exchange, dissolution of minerals, sorption-desorption of solutes, and mobilization of metals.

Samples of ground water will be collected and analyzed. Special analyses for unstable constituents will be conducted in the field. In addition, gases and stable isotopes (C, H, O) will be analyzed in selected samples. Aquifer materials will be analyzed by x-ray diffraction and scanning electron microscope for semiquantitative bulk mineralogy and clay mineral speciation. In-situ coatings on mineral grains and pore space distribution will be examined petrographically in thin-section. Data on sediment coatings and sediment chemistry (x-ray fluorescence) will be collected.

Hypothesis 2.—Organic solutes (contaminants) are differentially retained or sorbed during ground-water transport.

High performance liquid chromatography, gas chromatography, and GC-mass spectrometry will be used to analyze water and aquifer sediments for wood-treating chemicals and metabolites. Sorption data for pentachlorophenol and selected phenolic and polynuclear aromatic solutes will be obtained from laboratory column experiments on selected aquifer sediments. The differential movement of phenolic compounds, polynuclear aromatic compounds, pentachlorophenol and other organic solutes at ACW will be compared to results from laboratory column studies on sorption.

Microbiology

Hypothesis 1.—Bacteria are responsible for the observed loss of phenolic compounds.

Of the dozen or so compounds that make up the bulk of the phenolic component of the pollutant load at ACW only phenol, 3-methylphenol, and 4-methylphenol and possibly 2, 5, and 3, 4-demethylphenol have been shown to be substrates for methanogenic fermentation in laboratory studies. To determine the pathways of degradation, methanogenic populations of the bacterial consortium selectively inhibited in digestors. The digestor will be incubated and periodically analyzed for changes in chemistry that may indicate the mechanism for degradation.

In-situ rates of the degradation and pathway(s) of phenol will be estimated by measuring the conversion of radioactive labeled C^{14} -phenol in spiked core samples to C^{14} -methane and C^{14} carbon dioxide.

Hypothesis 2.—Pentachlorophenol and creosote inhibit the degradation of phenolic compounds.

The pollutant load under the ponds includes aqueous phase pentachlorophenol and creosote, and presumably a polynuclear aromatic rich organic nonaqueous liquid (NAPL). Results of a laboratory study now underway show that methanogenic fermentation of phenolic compounds is inhibited at pentachlorophenol concentrations of 1.0 milligram per liter (mg/L) in parts of the aquifer at ACW, but the inhibitory effects of other compounds present in creosote on the methanogenic fermentation of phenolic compounds is unknown. A dilution series will be set up in the laboratory to determine at what concentrations and over what time frame pentachlorophenol and other compounds in creosote inhibit methanogenic fermentation of phenols. This experiment will also analyze the inhibitory effects of water soluble compounds versus that of the NAPL.

Hypothesis 3.—Alkyl phenols are first de-alkylated by a sequential mechanism to phenol which is the common substrate for methanogenic bacteria.

To further elucidate the operation and extent of the bioreactor at ACW, we propose to study the bacterial communities in water and core samples from the area where reactions involving the apparent recalcitrant compounds are occurring.

Data on degradation rates and pathway(s) from laboratory experiments will be compared to data obtained from samples at the ACW site.

Hypothesis 4.—Mechanisms other than dilution contribute to a reduction in contaminant concentrations in the stream (drainage) system.

A mass balance approach will be taken in assessing the mechanisms and characterizing the processes contributing to a reduction in contaminant concentrations in the stream. Sampling sites will be selected at the headwaters, and at two or three other midpoint and downstream locations on the stream and loads of selected organic and inorganic contaminants measured during steady-state conditions. A mixing model will then be used to assess if the changes in concentration at sampling points can be accounted for by dilution or if other mechanisms are involved. Additional research will be conducted to define the changes in water quality that occurs as a result of the discharge of contaminated ground water to surface water.

Macrobiology

Hypothesis 1.—Organisms exhibit lower diversity but greater biomass of benthic fauna in areas of Pensacola Bay and Bayou Chico where contaminants in creosote and pentachlorophenol are found above natural levels in water and sediments.

Analysis of benthic community structure will be conducted for sites in and near Bayou Chico. A control site in Pensacola Bay but distant from Bayou Chico will be used for comparison. The results of this community structure analysis will be used to identify a widely distributed index organism suitable for tissue analysis. Samples of this organism will then be collected and separated into size classes, if necessary.

REGIONAL GROUND-WATER QUALITY STUDIES

A significant body of ground-water information exists concerning hydrogeologic setting and inorganic water quality of many ground-water systems in the Nation. The information was developed by local, State, and Federal agencies, and by numerous studies performed as part of the Federal and Federal-state cooperative programs in the Water Resources Division of the USGS. The information has provided a basis to judge some of the effects of human activities on ground-water resources, at least in terms of the relative degree of susceptibility to contamination, and an understanding of the relative impact of point and non-point sources of contamination.

However, the data base is lacking in adequate information concerning organic substances, trace metals, and other important parameters for ground water. Thus, no definition of baseline for these constituents is available, nor is there any way to make reasonable estimates of the extent or trends of ground-water contamination from these substances. Consequently, the following often-asked questions cannot be answered confidently.

- To what extent is our ground water contaminated?
- Is it getting better or getting worse?
- What activities have the greatest impacts on ground-water quality?

Objective

The objective of the regional Ground-Water Quality Studies is to assess the present quality of the Nation's ground-water reserves and the nature and extent of the ground-water contamination problem. This will be done by intensive study of individual areas that are representative of wider regions in terms of climate, ground-water hydrology, and human activities.

The objective of the individual studies is, (1) to provide information on ambient ground-water chemistry with emphasis on organic substances and trace metals in order to explain the chemistry in terms of the local hydrology and human activities, and (2) to identify those conclusions and principles which are applicable to similar areas elsewhere.

Approach

Study-Area Selection Criteria

Selection of study areas will occur in fiscal year 1984. Each study area will be representative of a common or significant climatic and geohydrologic environment. For example, a study area might represent a carbonate-rock aquifer system in an arid environment, or glacial valley aquifers in a humid and temperate climate, or so on. The entire set of study areas will cover the range of major climatic and geohydrologic classifications recognized in the Nation.

Study areas may vary in size from a few tens of square miles to a few thousand square miles. Regardless of the scale, each area should be characterized by internally uniform climatic and geohydrologic conditions. The general hydrology and ground-water flow system in the study area should be well understood, and there should be a reasonable body of available data on ground-water quality.

Each study area will include more than one type of land-use subarea. The transitions from one land-use subarea to another should be well defined so that correlations between ground-water quality and land use can be established. For example, a given study area might include agricultural and residential subareas, or might include residential, industrial, and mining subareas. The entire set of study areas should cover all of the major recognized land classifications, including irrigated cropping, nonirrigated cropping, livestock, sewered residential areas, unsewered residential areas, light and heavy industry, active and abandoned mining areas, petroleum production, undisturbed natural areas, and so on. The set of study areas should be chosen in such a way that each land use is studied in several different geohydrologic and climatic settings.

Protocol of Study

Each study will begin with an effort to refine understanding of the ground-water system by assembling existing hydrologic, geologic, and water-quality information, and pertinent land use, and related cultural information. The scale of the effort will vary according to what has been done in the past. In some cases, very little may be required. In others, ground-water models may have to be constructed or updated, and simulations carried out to define ground-water flow patterns in sufficient detail to support water-quality studies. Existing data on ground-water quality and contamination will be assembled, evaluated, and entered in automated data systems as appropriate to the needs of the study. This information will generally include chemical analyses of water from wells and springs, analyses of water from surface-water bodies which recharge or drain the ground-water system, and information on nonpoint and point sources of contamination. Using the assembled water-quality information in conjunction with information on ground-water flow patterns, studies will be designed to assess the factors affecting ground-water chemistry. Further analysis and additional data collection will then be undertaken to refine and extend our knowledge of ground-water quality.

Studies will begin with a reconnaissance phase that uses direct- and, when practical, indirect-sampling techniques such as surface geophysics and gas "sniffing" to determine if major water-quality zones in the study area coincide with land-use subareas. Water samples will be collected to determine general and colligative properties—to measure total hydrocarbon concentrations or other non-compound specific parameters, such as gas chromtograph flame ionization detector scans.

The ranges in total organic concentration and the gas chromatograph "fingerprint" of the organic substances present will aid in determining an appropriate sampling network for the entire study area and for the land-use subareas.

Following reconnaissance, water samples will be collected for analysis of the major classes of organic compounds, trace metals, microbiota, common constituents and other relevant parameters. Although the study will primarily use water samples to characterize ground-water quality, core samples will be collected to examine solid-phase characteristics, to determine the presence of hydrophobic chemical species, to assess the affect of biotic process on water quality, and other influences of the solid phase on aqueous chemistry.

Spatial and temporal variability of the data will be determined using graphical and statistical methods. Changes in the concentrations of organic substances and other constituents with depth will be defined whenever possible.

Emphasis will be placed on interpretations concerning the current state of the shallow aquifer systems underlying the different land uses. Hypotheses concerning the correlation between land use and ground-water quality will be evaluated through a variety of statistical methods. In conjunction with ground-water models, interpretations will be made of the avenues for contamination and processes affecting changes of contaminant concentration. Potential future impacts on both ground and surface waters in the system will be analyzed. Deeper aquifers also will be sampled to determine their vulnerability to contamination from surface of shallow ground-water sources. To the extent feasible, results from the areal studies will be related to other similar areas to make regional and national interpretations.

Based on results of the first appraisals, the sampling networks and data-collection activities will be modified to improve results and cost-effectiveness. Additional sampling and analyses will be scheduled for future years to determine long-term change. The frequency of future samplings will depend on such factors as hydrogeologic setting, land-use types, and changes in land use.

FUTURE DIRECTIONS

In FY 84, the Subsurface Waste Program of the USGS will be merged into the Toxic Waste—Ground-Water Contamination Program to provide an even better focus for studies of the emplacement, storage, and movement of hazardous substances in the subsurface. In FY 84, process-oriented research will be expanded to include additional research studies in such subjects as organic and inorganic geochemistry, borehole geophysics, and surface-water geochemistry.

Problem-oriented studies will continue at the Bemidji, Minnesota; Cape Cod, Massachusetts; and Pensacola, Florida field sites. Additional sites are being evaluated to study the fate of gasoline, agricultural chemicals, metals and chlorinated hydrocarbons. Sampling and analytical methods will be evaluated to ensure that representative samples of ground waters can be obtained. Regional ground-water quality appraisals will begin in FY 84. It is expected that ten to twenty regional studies will be initiated.