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TOXIC SUBSTANCES HYDROLOGY PROGRAM

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By Gail E. Mallard and David A. Aronson, compilers

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PREFACE

The U.S. Geological Survey's Toxic Substances Hydrology Program provides earth-science information needed to understand the movement and fate of hazardous substances in the Nation's ground and surface waters. To do this, the program (1) conducts laboratory and field research on the physical, chemical, and biological processes controlling contaminant transport and transformation; (2) develops new analytical methods and sampling techniques; and (3) investigates the relations among various human activities, environmental characteristics, and regional patterns of water quality.

The latest results of research conducted by the Toxic Substances Hydrology program were presented at a technical meeting held in Monterey, California, in March 1991. This report contains the abstracts of oral and poster presentations given at the Monterey meeting. To ensure that the abstracts would be ready for distribution at the meeting, they were reproduced as submitted by the authors. Time did not permit preparation of the abstracts in a uniform format.

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OVERVIEW OF RESEARCH AT THE CAPE COD SITE: FIELD AND LABORATORY STUDIES OF HYDROLOGIC, CHEMICAL, AND MICROBIOLOGICAL PROCESSES AFFECTING TRANSPORT IN A SEWAGE-CONTAMINATED SAND AND GRAVEL AQUIFER

by Stephen P. Garabedian[1] and Denis R. LeBlanc[1]

The Cape Cod Toxic-Substances Hydrology Research site, located in Falmouth, Massachusetts, is the focus for a number of field research projects studying subsurface contaminant hydrology, inorganic and organic geochemistry, and microbiology. Past research efforts at the site have involved definition and description of the extent of aquifer contamination in a sewage plume originating from the Otis Air Base sewage-treatment facility. Current research at the site is reviewed in a synopsis of 25 papers. These papers include efforts to characterize specific physical, chemical, and microbiological processes affecting the transport and fate of solutes and bacteria at the site. These processes are characterized using small-scale laboratory experiments such as batch and column tests, intermediate-scale field experiments such as natural-gradient tracer tests with transport distances of 1 to 280 meters, and large-scale investigations of the sewage plume with specialized sampling methods.

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BACKGROUND AQUEOUS CHEMISTRY OF SHALLOW GROUND WATER IN A SEWAGE-CONTAMINATED GLACIAL OUTWASH AQUIFER, CAPE COD, MASSACHUSSETTS

by Roger W. Lee
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ABSTRACT

Chemical data were collected in 1988-89 from 36 wells representing 18 uncontaminated sites in the vicinity of a sewage plume emanating from disposal areas at Otis Air Base. These samples had low concentrations of dissolved solids (generally less than 150 milligrams per liter); pH, and concentrations of dissolved solids and silica generally increased with depth in the aquifer. Although road-salting practices appear to have added solutes to shallow ground water at a few locations, this practice did not affect ground water at three sites where concentrations of dissolved solids decrease with increasing depth. A geochemical model using the computer code PHREEQE matches observed chemical data with chemical reactions that involve incongruent dissolution of feldspar minerals to kaolinite, and dissolved CO_2 in recharge water, that varies from about 0.05 to 0.4 millimoles per liter. This result suggests that a non-uniform distribution of CO_2 may exist in the unsaturated zone in the study area. The various land-use practices and surface features, such as residential subdivisions, golf courses, large cultivated grass fields, kettle ponds, and conifer forests each may cause variations in the production of CO_2 or in the flux of CO_2 from the unsaturated zone into the water table aquifer.

EFFECT OF THE GEOCHEMICAL ENVIRONMENT ON HEAVY-METAL TRANSPORT IN GROUND WATER

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ABSTRACT:

An overview is presented of a field-based research program that is examining the significance of chemical reactions in toxic-metal transport in ground water. Both natural-gradient tracer tests and laboratory experiments with subsurface materials are being used to evaluate the relative importance of hydrologic and geochemical processes affecting metal transport. The experiments are being conducted in an uncontaminated, recharge zone and in sewage-contaminated zones of the sand and gravel aquifer at the Cape Cod Toxic-Substance Hydrology Research Site. The results of tracer tests with zinc, chromium, and selenium showed that various chemical processes can have a dominant effect on metal transport; these processes include oxidation-reduction, adsorption-desorption, and aqueous complexation reactions. In some cases, significant speciation changes occurred as the injected tracers moved downgradient, and the changes generally had marked effects on the reactivity of the tracers with the porous medium. The experiments revealed that equilibrium geochemical models will be difficult to apply in modeling the transport of some redox-sensitive contaminants, such as chromium(VI) and selenium(VI), because of the specific nature of interactions of each element with reductants. A practical modeling approach for describing metal transport in ground water may require properly designed laboratory experiments in order to identify and minimize the number of chemical reactions considered in a hydrogeochemical transport model.

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BIOGEOCHEMICAL FATE OF ORGANIC COMPOUNDS IN SEWAGE CONTAMINATED GROUND WATER, CAPE COD, MASSACHUSETTS

by Larry B. Barber[1], E. Michael Thurman[2], Jennifer A. Field[3], Jerry A. Leenheer[1], Denis R. LeBlanc[4], Richard L. Smith[1], and Ronald W. Harvey[5]

ABSTRACT

The occurrence and distribution of organic compounds in the ground-water contamination plume at the Cape Cod Toxic-Substance Hydrology Research Site, located near Falmouth, Massachusetts, has been the subject of intensive study since 1983. The results of this effort provide insight into the biogeochemical processes controlling the fate and transport of sewage-derived contaminants in ground water. The plume of contamination, resulting from disposal of secondary-sewage effluent into a sand and gravel aquifer, is very complex and a hierarchical analytical approach is required to measure the wide range of organic compounds present. Major organic contaminants that have been identified include: (1) volatile chlorinated hydrocarbons (VCHs); (2) anionic and nonionic surfactants; and (3) biological metabolites of anionic and nonionic surfactants. The VCHs, which include di-, tri-, and tetrachloroethene, do not appear to undergo biodegradation or sorption to the aquifer sediments. Their distribution probably results from variation in the chemical composition of the effluent over time. In contrast, the occurrence and distribution of anionic and nonionic surfactants appear to be controlled by biodegradation and sorption. Anionic surfactant biodegradation is indicated by significantly diminished concentrations in the ground water relative to the sewage effluent and the presence of metabolic intermediates in the ground water. Because of the increased polarity and solubility of the metabolites with respect to the parent compound, they are not significantly sorbed by the aquifer sediments. Nonionic surfactant biodegradation also is indicated by diminished concentrations in the ground water and the appearance of biological metabolites. However, in contrast to anionic surfactants, nonionic surfactant biodegradation results in compounds that are less soluble than the parent compound, and transport of the degradation products appears to be retarded by sorption to the aquifer sediments.

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EFFECTS OF DENITRIFICATION ON NITROGEN GEOCHEMISTRY IN A NITRATE-CONTAMINATED SAND AND GRAVEL AQUIFER, CAPE COD, MASSACHUSETTS

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ABSTRACT

A relatively narrow vertical zone (5-6 meters thick) of nitrate (NO_3^-)-containing ground water was identified using multilevel sampling devices within an unconfined sand and gravel aquifer located on Cape Cod, Mass. The aquifer has been contaminated by surface disposal of treated sewage 0.3 kilometers upgradient from the study area. The NO_3^- zone was anoxic, contained high concentrations of nitrous oxide (16.5 micromolar), and coincided with a zone of active denitrification. Concentrations of nitrogen gas (N_2), the principal product of denitrification, were close to atmospheric equilibrium in uncontaminated ground water, but were significantly higher within the contaminant plume. The amount of excess N_2 was used to calculate the amount of nitrate reduced within a given transport interval. Denitrification resulted in an increase in the natural $\delta^{15}N$ of NO_3^- (from +13.6 to +42.0 per mil) and N_2 (+11.2 per mil per millimole per liter of N_2 produced) due to kinetic fractionation. The isotopic enrichment factor for in-situ denitrification was determined to be -13.9 per mil. These results demonstrate that denitrification can have a significant effect upon the geochemistry of ground water, but that closely spaced vertical sampling is necessary to study the process within aquifer environments.

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THE ROLE OF PHYSICAL AND CHEMICAL HETEROGENEITY IN THE INTERPRETATION OF SMALL-SCALE TRACER TESTS INVOLVING MICROORGANISMS

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ABSTRACT

Transport of microorganisms in contaminated groundwater is best studied in-situ, because it is difficult to duplicate in-situ conditions in the laboratory and the repacking of aquifer material into columns can significantly alter pore structure. A series of small-scale (6 to 12-m [meters] travel distance), natural-gradient tracer experiments have been conducted at different locations and depths within an organically-contaminated (treated sewage) section of the aquifer that had been instrumented with a 20 by 220 m array of 15-port, multilevel samplers. The instrumented study area is part of the U.S. Geological Survey's Cape Cod Toxic-Substances Research Site, located in Falmouth, Massachusetts. These tests have allowed assessment of differences in transport between various microorganisms, microspheres, and conservative tracers within different zones of the aquifer. Substantial differences in the relative transport between bacteria and microspheres and between bacterial-sized colloids and the conservative tracers were observed among sites; In some cases, these differences limited the transferability of models used to describe the downgradient bacterial migration. Therefore, interpretation can be complicated by physical and chemical heterogeneity, even though small-scale in-situ experiments provide more realistic information than do flow-through column studies. Comparisons of similar experiments performed at different locations and at different depths within the aquifer suggest that the effects of physical and chemical heterogeneity (grain size distribution, preferred flow-path pore structure, ground-water chemistry and mineralogy) upon observed transport of microorganisms and microbially-important substances need to be taken into account to describe the relative contributions of individual processes to bacterial transport.

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RESEARCH IN FRACTURED-ROCK HYDROGEOLOGY: CHARACTERIZING FLUID MOVEMENT AND CHEMICAL TRANSPORT IN FRACTURED ROCK AT THE MIRROR LAKE DRAINAGE BASIN, NEW HAMPSHIRE

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ABSTRACT

Many scenarios of anthropogenic waste isolation consider burial in unconsolidated near-surface deposits; however, these wastes can leach into the underlying bedrock. Fractures in the bedrock have the capacity to transport contaminants rapidly over large distances, and therefore, can have a great effect on ground-water and surface-water resources. Prediction of fluid movement and chemical transport in fractured rock is a complex task because of the difficulty in physically identifying and mathematically characterizing the spatial variability of hydraulic properties of the bedrock over various length dimensions. This problem is encountered in all subsurface flow regimes, but it is most acute in fractured rock because of the extreme spatial variability and the abrupt spatial changes in hydraulic properties. These conditions make it difficult to design field experiments and to employ interpretative methods of predicting fluid movement and chemical transport that were developed for application to unconsolidated porous media. To address these problems in fractured-rock hydrogeology, a multidisciplined research project is being conducted in the bedrock of the Mirror Lake drainage basin in the Hubbard Brook Experimental Forest in central New Hampshire.

The principle objectives of this study are to: (1) develop methods of monitoring hydraulic and chemical information in heterogeneous bedrock flow regimes; (2) develop hydraulic, tracer, geophysical and geochemical field techniques and interpretative methods to identify hydraulic and transport properties of bedrock and to characterize fluid movement and chemical transport over various length dimensions; (3) improve upon interpretative models of fluid movement and chemical transport in bedrock by incorporating geologic, lithologic and fracture mapping information; and (4) establish a site for long-term monitoring of bedrock environments and a controlled field-scale laboratory to test new equipment and interpretative analyses for characterizing and predicting fluid movement and chemical transport in fractured rock.

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COMPARING GEOPHYSICAL LOGS TO CORE AND CROSS-HOLE FLOW LOGGING IN THE MIRROR LAKE DRAINAGE BASIN

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ABSTRACT

An ongoing fracture-flow study based on geophysical log analysis and other geophysical and hydrologic techniques was expanded by adding additional boreholes to an existing experimental well field in the Mirror Lake watershed. One of these new boreholes was cored in order to compare lithologies and fractures identified on cores with those inferred from geophysical logs. Comparison of cores with geophysical logs confirms the accuracy of interpretation of generalized lithology and fractures on the basis of geophysical logs alone. However, the logs did not indicate some of the minor, possibly closed in-situ fractures seen in the recovered cores. At the same time, one of the largest and most permeable fractures indicated by the geophysical logs was not observed in the core. The original boreholes in the experimental well field were shown to intersect a highly conductive zone formed by the intersection of numerous discrete and discontinuous fractures. Cross-borehole pumping tests demonstrate that the highly conductive zone identified in previous studies intersects the core hole, but not the other new boreholes indicating the discontinuous and heterogeneous nature of permeable zones in bedrock at this site.

EXAMINATION OF HEAD DATA
IN A FRACTURED AND LAYERED SYSTEM,
ROCK SPRINGS, WYOMING

By Kathy Muller Ogle[1]

ABSTRACT

The White Mountain in-situ oil-shale retort area was a U.S. Department of Energy test site for burning oil shale in place to evaluate methods of oil extraction without removal of the shale. The area is 7.5 miles west of Rock Springs, Wyoming. The Tipton Shale Member of the Green River Formation (Eocene) at site 9 in the White Mountain area was retorted in 1976 to extract oil.

Head values indicate a complex ground-water-flow system at White Mountain area in the vicinity of site 9. Annual temporal water-level fluctuations of 5 to 10 ft (feet) were observed in monitoring wells completed in four different stratigraphic intervals. The potential for flow to the 10-ft-thick Tipton Shale Member layer, correlating to the lower one-third of the retort chamber, from the overlying 8-ft-thick sandstone layer is indicated by differences in head. Spatial variability indicates a potential for horizontal flow to the southwest and west within the 10-ft-thick Tipton Shale layer. The causes of the fluctuations in head have not been determined. However, a dynamic system is indicated by the head data.

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Geographic and Temporal Distribution of Herbicides in Surface Waters of the Upper Midwestern United States, 1989-90

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ABSTRACT

Results from a 2-year study of 149 streams geographically distributed across the corn-producing region of 10 midwestern States show that detectable concentrations of herbicides persist year round in most streams. During late spring and summer, concentrations of one or more herbicides exceeded U.S. Environmental Protection Agency proposed maaximum contaminant levels (PMCLs) for drinking water in more than one-half the streams sampled. Some herbicides exceeded PMCLs during runoff for periods of several weeks to several months. Atrazine was the most frequently detected and most persistent herbicide measured, followed by desethylatrazine (an atrazine metabolite) and metolachlor. Alachlor and cyanazine were detected primarily during the late spring and summer. The seasonal distribution of atrazine indicates that aquifers contributing base flow to the streams are contaminated with herbicides. Results from this study, which are believed to be applicable to other streams throughout the upper Midwest, indicate an annual cycle of herbicide application, a series of flushing events during which herbicides are transported into streams and ground water, and periods of base flow during which persistent herbicides are discharged into the streams from ground-water sources.

SOURCE OF ATRAZINE, DESETHYLATRAZINE, METOLACHLOR IN A SELECTED REACH OF THE CEDAR RIVER, IOWA, DURING BASE-FLOW CONDITIONS

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ABSTRACT

A budget of atrazine, desethylatrazine, and metolachlor loads was computed for a 116-kilometer reach of the Cedar River in Iowa to determine where these compounds enter the river during base flow conditions. Loads were determined by measuring discharge and concentrations of the compounds for four main-stem sites along the Cedar River and for 27 tributaries on September 20-22, 1989. Tributaries contributed 17 percent of the increased atrazine load, 24 percent of the increased desethylatrazine load, and 38 percent of the increased metolachlor load measured between the extreme upstream and downstream sites on the Cedar River. The remaining 62 to 83 percent of the increased loads is attributed to input along the rivers' main stem. Ground-water discharge carrying atrazine and desethylatrazine is a likely source of some of the increased load detected in the river for two reasons: (1) Measurable increases of atrazine loads were associated only with those reaches of the river where discharge substantially increased because of ground-water discharge, (2) the mean concentrations of both atrazine (0.27 µg/L (micrograms per liter)) and desethylatrazine (0.11 µg/L) in 15 shallow ground-water samples were equal to measured concentrations in the river 6 and 10 days after the ground-water samples were collected. The ground-water samples were collected from depths from 1 to 2 meters beneath the river bottom where the ground water was determined to be moving toward the river. The sources of atrazine and desethylatrazine detected in this ground water may include bank storage of river water, desorption of chemicals on sediment in the alluvial aquifer, or ground water originating at some distance from the river.

THE EFFECT OF SURFACE-WATER AND GROUND-WATER EXCHANGE ON THE TRANSPORT AND STORAGE OF ATRAZINE IN THE CEDAR RIVER, IOWA

by Michael J. Liszewski[1] and Paul J. Squillace[1]

ABSTRACT

The transport and storage of atrazine was studied in the Cedar River and an adjacent alluvial aquifer in eastern Iowa. River samples were collected monthly during low-flow conditions from May through December 1989, and daily during the rise and fall of the river stage caused by storm runoff in March 1990. Water samples were collected from 23 wells completed in the aquifer in a vertical plane 150 meters long by 15 meters deep and perpendicular to the river. The wells were sampled five times during low-flow conditions of the Cedar River during 1989 and three times over the rise and fall of the river stage caused by storm runoff in 1990.

Atrazine concentrations in the Cedar River ranged from 0.12 μg/L (micrograms per liter) during extended low-flow conditions begining in July 1989 to 0.82 μg/L during peak river stage in March 1990. Atrazine concentrations in samples from wells in the alluvial aquifer ranged from less than 0.05 μg/L to 0.68 μg/L during the period of study. In general, atrazine concentrations were stratified in the alluvial aquifer with greater concentrations occurring near the top. The period of high river stage in March of 1990 correlates with large concentrations of atrazine in samples from wells less than 30 m (meters) from the river. Concentrations of atrazine in samples from the wells greater than 30 m from the river did not correlate to the high river stage.

The observed data may be explained by the exchange of surface water and ground water in the adjacent alluvial aquifer as a result of changes in river stage during periods of storm runoff and low flow. The data suggest that the alluvial aquifer may act as a reservoir of atrazine. During storms, areas of the aquifer closest to the river are recharged with river water containing atrazine, which may later return to the river during low flow. Water-table gradients and specific-conductance measurements provide evidence for (1) a large ground-water component in the streamflow during low-flow conditions, and (2) the presence of infiltrated river water in the aquifer during high river stage.

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[1] U.S. Geological Survey, Iowa City, Iowa.

Dissipation of Starch Encapsulated Herbicides: A Field Comparison with Powdered Herbicides.

by

M. S. Mills[1], E. M. Thurman[1], R. E. Wing[2], and P. L. Barnes[3]

ABSTRACT

A dissipation study of atrazine and alachlor in starch-encapsulated and powdered forms was conducted on two adjacent corn plots at the Silver Lake Experimental Field Site, near Topeka, Kansas. A 30-percent difference in the total mass of herbicide washed from the plots was observed and attributed to the different release patterns of the two herbicide forms. The distribution of mass of starch-encapsulated herbicide released in runoff water throughout the growing season followed a normal-distribution-shaped curve, whereas the powdered-herbicide runoff water had a high mass present at the start of the season, which decreased in an exponential manner through time. Atrazine and alachlor were released slowly from the starch-encapsulating matrix as it expanded in the presence of water, and only a small mass of herbicide was present at any time for wash-off, throughout the entire runoff season. Because of this slow release of starch-encapsulated herbicides, the initial flush of large concentrations of herbicides from fields could be reduced by a factor of approximately 20, and decrease the total mass of herbicide washed from the field by 30 percent. Furthermore, the slow release of encapsulated herbicides should extend the residence time of the parent herbicide in the microbially active top-soil zone, which enhances biological and chemical degradation to less-active metabolites while maintaining weed control.

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SPATIAL VARIABILITY IN HYDRAULIC CONDUCTIVITY OF A SILT-LOAM SOIL NEAR TOPEKA, KANSAS

By David A. V. Eckhardt[1] and Philip L. Barnes[2]

ABSTRACT

A soil's hydraulic conductivity can be estimated fairly accurately from undisturbed profiles under conditions of steady-state ponded infiltration by monitoring the drainage and redistribution of soil water in the profile after cessation of infiltration. An exponential relation of unsaturated soil hydraulic conductivity [$K(\theta)$] to water content (θ) is assumed in the form of

$$K(\theta) = K_0 \cdot \exp[\beta(\theta - \theta_0)],$$

where K_0 is the hydraulic conductivity during steady-state ponded infiltration,
θ_0 is the corresponding soil-water content during steady-state ponded infiltration, and
β is a dimensionless constant.

In this study, the spatial distributions of β and K_0 at selected depths were determined by measurements of soil-water content after the cessation of infiltration ($\theta_0 - \theta$) over time at each of eight depths at 18 locations in a 0.75-hectare silt-loam plot near Topeka, Kansas. Values of β and K_0 for 133 of the measurements were approximately log-normally distributed about their means. Mean β was 74, and mean K_0 was 0.12 cm/hr (centimeters per hour). The values of K_0 and β measured at one site were used in a numerical unsaturated flow model to simulate decreasing water content in the soil profile during drainage. Model results indicate that the field method provides reasonable estimates of K_0 and β and that simplifying assumptions were accurately met. Differences between simulated and measured water contents in the selected soil profile are attributed to vertical variability in other soil physical properties, such as moisture-retention characteristics and bulk density, which would need to be quantified spatially to improve simulation.

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INTEGRATED HYDROLOGIC RESEARCH AT THE NORTHERN CORNBELT SAND-PLAIN MANAGEMENT SYSTEM EVALUATION AREA, MINNESOTA

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ABSTRACT

The U.S. Geological Survey (USGS), in cooperation with the U.S. Department of Agriculture and the U.S. Environmental Protection Agency (USEPA), is conducting interdisciplinary research on the effects of agricultural practices on water quality. A 0.65-square-kilometer site located near the town of Princeton, Minnesota, was selected for intensive research in the Anoka sand-plain aquifer to represent hydrogeologic conditions typical of the Midwest cornbelt sand plains. The site is adjacent to and upgradient from a stream and associated wetland. Material in the unsaturated and saturated zones at the site generally consists of fine-to-medium sand and medium-to-coarse sand, respectively. The saturated thickness of the aquifer is about 8 meters. The water table is from 0 to about 3 meters below land surface. The estimated horizontal hydraulic conductivity is about 10 centimeters per day.

The overall approach to conducting research at the Northern Cornbelt Sand-Plain Management System Evaluation Area is to identify and evaluate important processes and factors affecting the behavior and fate of agricultural chemicals in the environment. Multidisciplinary, multiscale research is planned for selected transport, transformation, and phase-transfer processes affecting the fate of agricultural chemicals in the various environmental compartments (atmosphere, soil/root zone, unsaturated zone, saturated zone, and surface water). The USGS Minnesota District will be coordinating physical and chemical hydrologic research and will provide logistical support for USGS and USEPA researchers at the Princeton site.

ESTIMATES OF GAS-PHASE PHOTOLYSIS FOR ATRAZINE, SIMAZINE, ALACHLOR, AND METOLACHLOR FROM EFFECTIVE ABSORPTION CROSS-SECTION MEASUREMENTS

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ABSTRACT

Ultraviolet-visible (UV-vis) absorption cross-sections, in conjunction with solar actinic-flux measurements, may be used to estimate effective photolysis half-lives of organic compounds in the troposphere. A scanning UV-vis spectrophotometer was used to measure the absorption cross-sections for wavelengths from 285 to 825 nm (nanometers), the region pertinent to solar photolysis of organic contaminants in the troposphere, for atrazine, simazine, alachlor, and metolachlor. The alpha-chloroacetamides, alachlor and metolachlor, were shown to have no absorbance in the wavelength region of solar actinic flux and, consequently, are expected to have extremely long photolysis half-lives in the troposphere. Small absorbances were observed in the range from 285 to 335 nm for atrazine and from 285 to 345 nm for simazine, indicating photolysis may occur for these two triazine herbicides in the troposphere. However, atmospheric reactions of all four herbicides with photochemical oxidants, like ozone and hydroxyl and nitrate radicals, may prove more important than photolysis as contaminant removal processes.

LITERATURE REVIEW OF VAPOR PRESSURE DATA FOR SOME CHLORINATED TRIAZINE AND ACETAMIDE HERBICIDES

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ABSTRACT

A comprehensive review of the literature has been undertaken to ascertain the original experimentally determined vapor pressure data for atrazine and four of its degradation products, desethylatrazine, desisopropylatrazine, desethyldesisopropylatrazine, and hydroxyatrazine, along with four additional herbicides, simazine, metribuzin, alachlor and metolachlor. Many of the reported vapor pressure values can be traced back to only one or two original experimental determinations. In other cases, the values given are incompletely cited. To date, only two citations containing original experimental data have been found for atrazine and one citation found for simazine. There appears to be no specific vapor pressure data available for any of the four major degradation products of atrazine. Vapor pressure data reported in the literature for alachlor, metolachlor and metribuzin appear to originate from manufacturer's data, the original experimental reports from which have not yet been ascertained.

Relation of Selected Water-Quality Constituents To River Stage In the Cedar River, Iowa

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ABSTRACT

Water samples collected from the Cedar River in east- central Iowa indicate that measured values of specific conductance and pH and concentrations of dissolved oxygen, nitrate, and atrazine are related to changes in river stage. Samples were collected monthly from May 1989 through July 1990; daily samples were collected during periods of storm runoff in March and May 1990. Specific conductance, pH, and concentrations of dissolved oxygen are apparently inversely related to the measured stage of the river, whereas concentrations of atrazine and nitrate are apparently directly related.

The apparent inverse relation of specific conductance to the measured stage of the river may be the result of the dilution of the ground-water component of river flow with surface-water runoff, which generally has less specific conductance and pH than ground water. The apparent inverse relation of pH and concentration of dissolved oxygen to the measured stage of the river may be the result of the dilution of dissolved oxygen and carbon dioxide in the stream by surface-water runoff.

Nitrate and atrazine concentrations, both of which are agricultural chemicals, correlated with time of application as well as with river stage. However, nitrate concentrations peaked several days after the peak stage of the river. These correlations may be the result of the leaching of these chemicals from agricultural areas during periods of storm runoff. Sample concentrations collected after application of the chemicals were larger than those collected before application.

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Photolytic Degradation of Atrazine in the Cedar River, Iowa, and its Tributaries, by Marvin C. Goldberg*, Kirkwood M. Cunningham*, and Paul J. Squillace**, U. S. Geological Survey P. O. Box 25046, MS 424, Denver Federal Center, Lakewood, Colorado 80225, **U. S. Geological Survey P. O. Box 1230, Iowa City Iowa 53344

One of the anthropogenic materials entering the Cedar River, Iowa, is atrazine. This herbicide is applied as an agricultural additive and as a consequence of rainfall-runoff, feeds into tributaries of the Cedar River, Iowa, from which it is carried to the mainstem of the river. Water samples collected from the tributaries and the mainstem were photolyzed in a sunlight simulator to evaluate the effect of sunlight induced degradation on this material as it is transported to the mainstem of the river. The loss rate of atrazine was measured as a function of photon flux and it was found that the half-lives of degradation, in midday sunlight at 40° lattitude, ranged from 38 to 318 hours at the 11 sites tested. A correlation was found between increased concentrations of nitrate and increased rates of photolytic degradation. Since nitrate is activated by sunlight to produce hydroxyl radical, the mechanism for photolytic decomposition is most likely an indirect photolysis where the nitrate ion is an intermediate sensitizer producing hydroxyl radical that then reacts with s-atrazine as follows:
.OH + Atrazine → 2,4-diamino-6-hydroxy-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine) + Cl
after several steps → Cyanuric Acid.
Photolytic degradation is site specific. Almost all of the photolytic degradation occurs in the tributaries. Very low rates of photolysis were measured in the mainstem. Nitrate is added to the natural environment in the form of fertilizer on a schedule determined by agricultural necessity; thus, both the occurrence and photolytic degradation of atrazine in tributaries to the Cedar River, Iowa, are controlled by agricultural perogatives.

MOVEMENT OF NITROGEN SPECIES AND HERBICIDES ON CLAYPAN SOILS AT THE MANAGEMENT SYSTEMS EVALUATION AREA IN MISSOURI

By
Dale W. Blevins[1]

ABSTRACT

Numerous studies of nitrogen, atrazine, and alachlor are being started by the U.S. Department of Agriculture and the U.S. Geological Survey at the Goodwater Creek basin in north-central Missouri. Claypan soils, loess, and glacial drift cover most of the basin. The primary crops are soybeans, corn, pasture, and wheat. Ground-water, surface-water, and water-quality data will be collected from study areas of 0.022, 1, 20 to 60, 3,200, 7,040, and 17,900 acres.

The large clay content of surficial materials in the basin premit macropore flow and provides an opportunity to conduct solute-transport studies. Other studies will determine the effects of three crop-management systems on the fate and transport of nitrogen species, alachlor, and atrazine. The U.S. Geological Survey will study the use of nitrogen and oxygen isotopes to trace nitrate from fertilizer through the unsaturated and saturated zones. Techniques to significantly decrease the cost of analyzing for nitrogen isotope ratios and to analyze oxygen-isotope ratios in nitrate will be developed.

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ISOLATION AND CHARACTERIZATION OF AUTOTROPHIC, HYDROGEN-OXIDIZING, DENITRIFYING BACTERIA FROM GROUND WATER AS POTENTIAL AGENTS FOR BIOREMEDIATION OF NITRATE CONTAMINATION

Richard L. Smith[1] and Marnie L. Ceazan[1]

ABSTRACT

Nitrate is a common contaminant of ground water in the United States due to agricultural practices and disposal of human and animal wastes. Nitrate is relatively stable, and therefore persistent, and is mobile in most aquifers. However, nitrate can be utilized by subsurface microorganisms. Denitrification is the microbial process most likely to remove significant quantities of nitrate from ground water because it is a dissimilatory process and it appears to be suitable as a mechanism for in-situ bioremediation because it produces an innocuous endproduct, nitrogen gas. The selection of an appropriate substrate to add to the subsurface to stimulate denitrification will be critical to its utility as a bioremediation process. Recently, incubations with sediments collected from a nitrate-contaminated aquifer on Cape Cod, Mass. demonstrated that the addition of hydrogen significantly stimulated denitrification. Subsequently, several strains of autotrophic, hydrogen-oxidizing bacteria were isolated from two different sites within the aquifer and then partially characterized. Although little is known about hydrogen oxidation by denitrification, this activity has significant potential for exploitation as a bioremediation process, and further characterization of these microorganisms is currently being conducted within that context.

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Survival of a Model Pollutant-Degrading Microorganism in a Sand and Gravel Aquifer and in Microcosms

By M. L. Krumme[1], R. L. Smith[2] and D. F. Dwyer[1]

ABSTRACT

In situ bioremediation may involve the addition into contaminated environments of non indigenous microorganisms that are capable of removing or degrading specific pollutants. Prior to their introduction into an environment, these microorganisms need to be assessed for their suitability as bioremediation agents and their potential to cause unwanted effects to that environment. We determined the usefulness of using microcosms to predict the in-situ fate of microorganisms added to aquifers by comparing the population dynamics of a model pollutant-degrading microorganism, Pseudomonas sp. B13 (B13) after introduction into laboratory microcosms and a sand and gravel aquifer. B13 was introduced into the aquifer in three depth intervals, where concentrations of dissolved oxygen (DO) were 10, 8, and 0 mg/L (milligrams per liter) and into microcosms, which contained aquifer core material from the same three depths. The B13 population was stable in all microcosms for 70 days after introduction. This was similar to results in the aquifer for two of the three depth intervals studied. In the depth interval where DO concentrations were 10 mg/L, the population of B13 was not detected 70 days after introduction.

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ADSORPTION AND REDUCTION OF Chromium(VI) UNDER OXIC CONDITIONS IN A SHALLOW SAND AQUIFER AT CAPE COD, MASSACHUSETTS

L.D. Anderson[1], D.B. Kent[1], and J.A. Davis[1]

ABSTRACT

Tracer injection studies indicate that reduction and adsorption of Chromium(VI) occurred in oxic sands but only reduction occurred in suboxic sands. Experiments with freshly collected core material and recharge water substantiated reduction by the oxic sands. Reductive potential is absent in aged, dried sands from both the oxic and suboxic core material, probably as a result of oxidation of sorbed or dissolved organic material and the surfaces of ferrous-containing minerals. Sorption on dried oxic core material was reversible (adsorption) and was less intense in the presence of increased sulfate. There was limited adsorption and no evident reduction on dried suboxic core material.

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REDUCTION AND TRANSPORT OF CHROMIUM(VI) UNDER MILDLY REDUCING CONDITIONS IN A SAND AND GRAVEL AQUIFER

J. A. Davis[1], T. D. Waite[2], D. B. Kent[1], and L. D. C. Anderson[1]

ABSTRACT

Field tracer tests and laboratory experiments with freshly collected glaciofluvial sediments have demonstrated that reduction of chromium(VI) [Cr(VI)] is a significant process controlling the mobility of Cr in the sewage-contaminated zone of the aquifer at the Cape Cod Toxic-Substances Hydrology Research Site. Removal of Cr(VI) from ground water in this suboxic zone occurred only by reduction to Cr(III), which was strongly and irreversibly sorbed. The effect of the chemical reactions on Cr(VI) transport is an attenuation of Cr mass transport relative to that of a nonreactive tracer. Interestingly, the attenuation is not accompanied by retardation in Cr transport. This occurs because all Cr(III) is rapidly and irreversibly sorbed, and Cr(VI) adsorption is negligible under the conditions present in the sewage-contaminated zone. The reduction process is highly pH-dependent, and the likely reductants are particulate organic carbon and the surfaces of ferrous-containing minerals, such as biotite and magnetite.

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SPATIAL VARIABILITY OF GEOCHEMICAL AND HYDROLOGIC PROPERTIES OF SUBSURFACE MATERIALS IN A SAND AND GRAVEL AQUIFER, CAPE COD, MASSACHUSETTS

by Christopher C. Fuller[1], Jennifer A. Coston[1], Kathryn M. Hess[2], and James A. Davis[1]

The effect of spatial variability in geochemical and hydrologic parameters on the transport of surface-reactive solutes in ground-water systems is being investigated in a shallow, sand and gravel aquifer on Cape Cod, Massachusetts. The focus of this study is to identify the geochemical processes controlling metal-ion sorption and to describe their spatial variability. The spatial variability of hydraulic conductivity estimated from grain-size distribution measurements also is being studied. The results will be used in conjunction with tracer-test studies of metal transport conducted at this site to develop coupled solute transport and reaction models that incorporate the observed spatial variability in geochemical properties used to estimate sorbent abundance, metal sorption coefficients, and hydraulic conductivity. The densely instrumented array of multilevel ground-water samplers at the research site at Cape Cod, Massachusetts, affords the opportunity for testing and refining transport models through field-scale tracer injection models. This paper outlines the objectives and approach of this research study. Sixty meters of core have been collected and the initial laboratory phase of this research has recently begun.

1. U.S. Geological Survey, Menlo Park, CA
2. U.S. Geological Survey, Marlborough, MA

MOBILITY OF ZINC IN A SEWAGE-CONTAMINATED AQUIFER, CAPE COD, MASSACHUSETTS

B.A. Rea[1], D.B. Kent[1], D.R. LeBlanc[2], and J.A. Davis[1]

ABSTRACT

Disposal of treated sewage effluent into the sand and gravel aquifer on Cape Cod, Massachusetts, has resulted in contamination of the aquifer with zinc (Zn). At sites up to 350 m (meters) downgradient from the disposal site, a zone of dissolved Zn is supported by a reservoir of adsorbed Zn. The contamination is limited to a 1- to 2-meter-thick zone at the upper margin of the sewage plume. At greater depths, the sewage plume is devoid of Zn, indicating that processes upgradient have lead to immobilizaton of Zn. Preliminary evidence supports the hypothesis that adsorption onto the aquifer material, which is complete at pH values characteristic of the sewage-contaminated zone, is the process responsible for immobilization. If true, there is a large reservoir of immobilized Zn in the vicinity of the disposal bed that could be mobilized by future changes in the aquifer chemistry.

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[1] U.S. Geological Survey, Menlo Park, Calif.

[2] U.S. Geological Survey, Marlborough, Mass.

TRANSPORT OF ZINC IN THE PRESENCE OF A STRONG COMPLEXING AGENT IN A SHALLOW AQUIFER IN CAPE COD, MASSACHUSETTS

D. B. Kent[1], J. A. Davis[1], L. D. Anderson[1], and B. A. Rea[1]

ABSTRACT

Small-scale natural-gradient tracer tests were performed in pristine and sewage-contaminated zones of a shallow, sand and gravel aquifer in Cape Cod, Massachusetts. Transport of tracers including zinc (Zn), ethylenediaminetetracetic acid (EDTA), and bromide ion (Br) was studied in each zone. In the sewage-contaminated zone, which had pH values near 6.0 and moderate concentrations of dissolved salt, Zn was transported conservatively as Zn-EDTA complexes. In the pristine recharge zone, which had pH values near 5.0 and low concentrations of dissolved salts, extensive retardation was observed. Retardation was probably caused by displacement of Zn from EDTA complexes by Fe(III) leached from aquifer material and extensive adsorption of Zn^{2+} ion, although adsorption of Zn-EDTA complexes could not be ruled out. Additional tracer tests have been performed to examine Zn and EDTA speciation; these results will aid in determining the predominant adsorption mechanisms. The results illustrate the importance of speciation and adsorption properties in controlling transport and how aquifer chemistry affects speciation and transport.

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1. U. S. Geological Survey, Menlo Park, CA

LABORATORY STUDIES OF BACTERIAL SORPTION TO AQUIFER SEDIMENTS FROM THE CAPE COD TOXIC-SUBSTANCES-HYDROLOGY SITE.

Martha A. Scholl and Ronald W. Harvey, USGS WRD, Menlo Park.

Field tests in the aquifer at the Cape Cod study site have shown that bacterial sorption to sediment surfaces is an important process affecting bacterial transport. A nonstirred batch method was used to study bacterial sorption in the laboratory under simulated aquifer conditions, using contaminated and uncontaminated ground water collected at the site. The pH-dependency of bacterial sorption and the degree of bacterial sorption to different surface types (untreated, organic matter removed, organic matter and oxyhydroxides removed) was determined in both types of ground water. Desorption of bacteria in the presence of phosphate buffer at pH 8 was shown to occur. The experiments indicate that geochemical conditions can affect bacterial mobility in the aquifer.

DEOXYRIBONUCLEIC ACID DISTRIBUTIONS AND RECOVERY IN ESTIMATION OF BIOMASS IN A SAND AND GRAVEL AQUIFER ON CAPE COD, MASSACHUSETTS

By David W. Metge[1] and Ronald W. Harvey[1]

ABSTRACT

A fluorometric-deoxyribonucleic acid (DNA) assay was evaluated for use in microbiological studies of sewage-contaminated aquifer sediments. Variations in quantity and in solute:solid and intracellular:extracellular partitioning of DNA were estimated in a 5-kilo-meter-long contaminant plume within a sand and gravel aquifer on Cape Cod, Massachusetts. These variations were correlated with ground-water chemistry and proximity to the source of contamination (on-land outfall for secondarily treated sewage). Most DNA (up to 99 percent) in the aquifer was particle-associated, and a surprisingly large fraction (up to 50 percent) of the DNA in contaminated aquifer sediments was extracellular and adsorbed. At some locations near the source of contamination, substantial fractions of porewater DNA were found to be associated with the protozoan-size fraction. Per-cell DNA content differed substantially among samples (2 to 14 and 2 to 20 femtograms per cell for adherent and free-living bacteria, respectively) and decreased with increasing distance from the contaminant source. In a separate study, an unidentified Pseudomonad bacterium isolated from the contaminant plume and grown in pure culture exhibited a 5-fold variation in per-cell DNA content in response to a 10-fold difference in growth rate. Several biotic and physical factors were found to affect the accuracy of the DNA assay for providing quantitative information involving bacterial distributions within aquifer sediments. Recovery of sediment-associated DNA depended on desorption conditions, mineralogy (sediment silt content), experimental protocol used, and bacterial lysis methodology.

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[1] U.S. Geological Survey, Water Resources Division, Menlo Park, Calif.

PRELIMINARY EVALUATION OF THE RELATIONS AMONG PROTOZOA, BACTERIA, AND CHEMICAL PROPERTIES IN SEWAGE-CONTAMINATED GROUND WATER NEAR OTIS AIR BASE, MASSACHUSETTS

by N. E. Kinner[1], A. L. Bunn[1], R. W. Harvey[2], A. Warren[3] and L. D. Meeker[1]

ABSTRACT

Protozoa have an important function in many surface water ecosystems, but have only recently been examined in aquifers. Preliminary studies suggested the presence of protozoa at the U.S. Geological Survey's Cape Cod Toxic-Substances Research site in Falmouth, Massachusetts. Because of the substantive background information on the hydrology, chemistry, and microbiology already collected at this site, a detailed study on the distribution, characterization, and ecological role of protozoa in the contaminant plume was started in 1990. The first phase of this research, which involved a plume-wide survey, revealed a large (more than 100000 individuals per gram in some samples) and active protozoan population in parts of the contaminant plume. The protozoa were quite small (2-5 micrometers in diameter) and appeared to be present in oxic and anoxic parts of the plume. Some of the protozoa were encysted. The abundance and distribution of the protozoa suggest they are an important feature of the microbiological community and may directly or indirectly affect the fate of at least some organic contaminants in the plume.

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[3] Natural History Museum, London

SIMULATION OF MOLYBDATE SORPTION WITH THE DIFFUSE LAYER SURFACE-COMPLEXATION MODEL

By Kenneth G. Stollenwerk[1]

ABSTRACT

Sorption of molybdate [Mo(VI)] as a function of aqueous and solid phase composition was evaluated in laboratory experiments. Sorption of Mo(VI) decreased as pH, sulfate (SO_4), and phosphate (PO_4) increased. Sorption of Mo(VI) increased with ferrihydrite content. Experimental data could be quantitatively modeled with the diffuse-layer surface-complexation model in the geochemical equilibrium speciation model MINTEQA2. Intrinsic acidity constants and intrinsic equilibrium constants for PO_4 sorption were obtained from the sorption literature. Intrinsic equilibrium constants for Mo(VI) and SO_4 were fit to experimental data: for Mo(VI), $\mathrm{Log}K_2^{int} = 8.0$ and $\mathrm{Log}K_3^{int} = -1.0$; for SO_4, $\mathrm{Log}K_2^{int} = 5.0$ and $\mathrm{Log}K_3^{int} = -0.4$. One set of equilibrium constants was used to simulate the experimental sorption data for the entire range of geochemical conditions that were considered.

[1] U.S. Geological Survey, Denver, Colo.

DESIGN AND OPERATION OF AN INFILTRATION EXPERIMENT IN UNSATURATED GLACIAL OUTWASH ON CAPE COD, MASSACHUSETTS

by Denis R. LeBlanc[1], David L. Rudolph[2], R. Gary Kachanoski[2,3],
and Michael A. Celia[4]

Flow and solute transport through the unsaturated zone were observed in detail during an infiltration experiment conducted in a sand and gravel glacial outwash on Cape Cod, Massachusetts. The objectives of the experiment were to test innovative field methods to measure flow and solute transport in the unsaturated zone and to improve understanding of unsaturated-zone hydrology in heterogeneous sediments. Soil-moisture content, pressure, and solute concentration were measured during a series of infiltration experiments conducted on a test plot 2 m(meters) wide and 10 m long. Instrumentation was installed to a depth of 2 m and included 168 pairs of time-domain reflectrometry probes and 112 suction-lysimeter/tensiometers. The 20-square-meter plot was irrigated through sprinkler nozzles set 1.5 m above ground surface. The experiments were divided into two sets. The first set focused on transport of solutes under steady-flow conditions with irrigation rates ranging from 7.9 to 37.0 centimeters per hour. The second set focused on transient water flow during several wetting and drying cycles. Analysis of the data will focus on spatial variability of the response of the unsaturated zone to irrigation and the ability of numerical models to simulate the experimental results.

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[4] Dept. of Civil Engineering and Operations Research, Princeton Univ., Princeton, NJ

DENSITY-INDUCED DOWNWARD MOVEMENT OF SOLUTES DURING A NATURAL-GRADIENT TRACER TEST ON CAPE COD, MASSACHUSETTS

by Denis R. LeBlanc[1] and Michael A. Celia[2]

Density contrasts can cause a plume of contaminated ground water to sink within an ambient flow field. Earlier studies had hypothesized that the downward movement of the bromide tracer cloud during the early part of a natural-gradient tracer test on Cape Cod, Massachusetts, was caused by density-induced sinking. Two analytical models of density-dependent flow were applied to the Cape Cod test to show that the density contrast between the ambient ground water and the tracer solution was sufficient to cause part of the observed sinking. The analytical models also illustrate that the amount of sinking depends on the anisotropy of hydraulic conductivity. A comparison of two- and three-dimensional analytical models for density-induced sinking suggests that predicted downward movement in the two-dimensional model is less than the movement predicted by the three-dimensional model of this fundamentally three-dimensional process. A numerical solute-transport model was used to show that downward movement increases with decreasing dispersion and increasing source size because both conditions serve to enhance the persistence of high concentrations in the solute cloud. The sensitivity to dispersion and the need to represent the system in three dimensions present computational difficulties for numerical simulations of density-dependent flow and solute transport.

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[2] Dept. of Civil Engineering and Operations Research, Princeton Univ., Princeton, NJ.

Estimation of Macrodispersivities from the Spatial Variability of Hydraulic Conductivity in a Sand and Gravel Aquifer, Cape Cod, Massachusetts

Kathryn M. Hess[a], Steven H. Wolf [b] and Michael A. Celia[c]

Spatial variability of hydraulic conductivity in a sand and gravel aquifer on Cape Cod, Massachusetts, was investigated in order to test stochastic transport equations relating macrodispersion to the statistical properties of the hydraulic-conductivity distribution. Nearly 1,500 measurements of hydraulic conductivity were obtained by borehole-flowmeter tests and permeameter analyses of cores. The geometric mean hydraulic conductivity from the flowmeter tests is 0.11 cm/s (centimeters per second) -- a rate similar to that estimated from a tracer test conducted at this site and an aquifer test conducted nearby. The geometric mean from the permeameter tests is 0.035 cm/s. This significantly lower value may result from compaction of the cores, nonrepresentative sampling, anisotropy of hydraulic conductivity, or a difference in averaging volumes between the two methods. The variance of the log-transformed hydraulic conductivity is also greater for the flowmeter values (0.24) than for the permeameter values (0.14). Geostatistical analysis of the hydraulic conductivities from the two methods reveals similar spatial-correlation structures; neither method detected any horizontal anisotropy. Isotropic horizontal correlation scales from variogram models with and without a nugget effect range from 2.9 to 8.0 m (meters); vertical correlation scales range from 0.18 to 0.19 m. A ratio of vertical to horizontal effective hydraulic conductivity of 1:1.2 is estimated by stochastic analysis. This ratio is slightly greater than previously reported ratios for the aquifer. Stochastic transport equations were also used to estimate asymptotic longitudinal macrodispersivities; these values, 0.35 to 1.4 m, are similar to the longitudinal dispersivity of 0.96 m observed in the tracer test. The predicted early-time development of the dispersion process indicates that a constant longitudinal dispersivity is reached quickly as was observed in the tracer test. The transport theories estimate that longitudinal dispersivity exceeds the transverse components, as was observed in the tracer test. However, the predicted transverse dispersivities (10^{-6} m) are lower than those observed in the tracer test (0.018 and 0.0015 m for the transverse horizontal and transverse vertical dispersivities, respectively). Incorporation of unsteady flow conditions increases the predicted value of transverse horizontal dispersivity to 0.024 m.

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PRELIMINARY DETERMINATION OF HYDRAULIC CONDUCTIVITY IN A SAND AND GRAVEL AQUIFER, CAPE COD, MASSACHUSETTS, FROM ANALYSIS OF NUCLEAR LOGS

Roger H. Morin[a] and Kathryn M. Hess[b]

An algorithm was developed to predict hydraulic conductivity from nuclear logs for a sand and gravel aquifer on Cape Cod, Massachusetts. Flowmeter tests conducted in long-screened wells at the site provided detailed vertical profiles of horizontal hydraulic conductivity, and nuclear logs provided quantitative estimates of porosity (neutron log) and qualitative indications of grain size (natural-gamma log) for 0.15-meter vertical sections of the aquifer. Because grain-size data were not available to develop a direct relation between grain size and gamma activity, hydraulic conductivities from the flowmeter tests and porosities from neutron logs were substituted into the Kozeny-Carmen equation to obtain estimates of grain size for three wells. A logarithmic relation between the square of the grain-size estimates and the gamma response was then developed. Representative values of grain size predicted by this relation and porosities obtained from neutron logs were then used to compute a vertical profile of hydraulic conductivity for a well that was not used to develop the algorithm. A comparison of predicted and observed hydraulic conductivities indicates that this preliminary algorithm was unable to reproduce the hydraulic conductivity profile accurately and needs to be refined. However, the algorithm did predict a hydraulic-conductivity distribution with a mean, variance, and vertical correlation scale similar to those of the observed distribution and, thus, may be useful in providing input parameters for the stochastic analysis of solute transport in the aquifer.

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CHARACTERIZATION OF LARGE-SCALE AQUIFER HETEROGENEITY IN GLACIAL OUTWASH BY ANALYSIS OF SLUG TESTS WITH OSCILLATORY RESPONSES, CAPE COD, MASSACHUSETTS

by Roland K. Springer[1] and Lynn W. Gelhar[1]

An extensive slug-testing program was carried out to characterize the large-scale spatial variability of hydraulic conductivity in glacial outwash on Cape Cod, Massachusetts. A secondary objective of the program was to determine the usefulness of slug tests for measuring hydraulic conductivity in very permeable sediments. A total of 338 observation wells were tested in a 17-square-mile area. Of these, 105 wells exhibited an oscillatory response to an instantaneous displacement of the water level. In order to be able to analyze all the slug tests, the method of Bouwer and Rice (1976) was modified to include inertial effects in the wells. This modification, which provides a treatment for oscillatory responses, yields hydraulic-conductivity values that are about 10 percent lower than values obtained by the method of Bouwer and Rice (1976) for the non-oscillatory case Preliminary analysis shows large variation in hydraulic-conductivity values, which range from 0.26 to 1,570 ft/d (feet per day) and have a geometric mean of 141 ft/d. The standard deviation of the natural logarithm of the hydraulic conductivity is 1.4. Results indicate a zone of low conductivity, less than 20 ft/d, located greater than 100 feet below the water table. Conductivity increases upwards, with zones of conductivity greater than 500 ft/d commonly located 25 to 60 feet below the water table.

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CHARACTERIZATION OF A SAND AND GRAVEL AQUIFER USING GROUND-PENETRATING RADAR, CAPE COD, MASSACHUSETTS

by M.D. Knoll[1], F.P. Haeni[2], and R.J. Knight[1]

ABSTRACT

Ground-penetrating radar was used to delineate near-surface geologic conditions in a sand and gravel aquifer on Cape Cod, Massachusetts, in 1990. Radar images yielded information on the overall radar character of the site, including the water table and depositional features in the aquifer to a depth of 40 feet. Some of the radar profiles were used to create a three-dimensional image of the aquifer. Preliminary experiments yielded average electromagnetic propagation velocities for the unsaturated and saturated zones of 0.45 ft/ns (feet per nanosecond) and 0.2 ft/ns, respectively. Quantitative analysis of the 1990 radar records is continuing, which will determine additional properties of the aquifer. In addition, the data set is being used to test new computer-processing techniques that will help visualize the subsurface.

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[2] U.S. Geological Survey, Hartford, Connecticut

Persistence of Linear Alkylbenzenesulfonates and their Metabolites in Sewage-Contaminated Ground Water

by

Jennifer A. Field[1], Larry B. Barber II[2], Jerry A. Leenheer[2],
Colleen E. Rostad[2], and Kevin A. Thorn[2]

ABSTRACT

Linear alkylbenzenesulfonates (LAS) are the most widely used surfactants in detergent formulations, and they are generally considered to be biodegradable. Although the fate of LAS during sewage treatment and their subsequent discharge into surface waters has been thoroughly investigated, few studies have focused on LAS transformation and transport in ground water. This study specifically investigated LAS transport and fate in a plume of sewage-contaminated ground water that has resulted from rapid infiltration of secondary-treated sewage to a sand and gravel aquifer.

A comprehensive approach involving reverse-phase and ion-exchange chromatography coupled with solvent extraction was used to isolate surfactant-derived contaminants from sewage effluent and ground water. Spectrometric methods, including infrared (IR), ^{1}H-nuclear magnetic resonance (NMR), ^{13}C-NMR, and gas chromatography/mass spectrometry (GC/MS) were used to identify surfactants and their biodegradation intermediates.

LAS and dialkyltetralin (and dialkylindane) sulfonates (DATS) were identified in sewage effluent and in ground water 500 meters downgradient from the point of effluent infiltration. Differences in LAS composition between sewage effluent and ground-water samples indicated preferential removal of external isomers and long-chain homologs during infiltration and ground-water transport. Monocarboxylated DATS and DATS biodegradation intermediates were also identified in sewage effluent and ground water. Results indicate that alicyclic contaminants (DATS and DATS-intermediates) are more persistent than their linear analogs. LAS half-life, estimated at 200 days, is an order of magnitude greater than laboratory-derived estimates for LAS biodegradation in ground water.

1. EAWAG, Dübendorf, Switzerland
2. U.S. Geological Survey, Denver, Colorado

PURGEABLE ORGANIC CHLORIDE- A SURROGATE MEASUREMENT FOR SCREENING AND MONITORING VOLATILE CHLORINATED HYDROCARBONS IN GROUND WATER

by

Larry B. Barber, II[1], E. Michael Thurman[2], Yoshi Takahashi[3], and Mary Noriega[1]

ABSTRACT

A combined field and laboratory study was conducted to compare results obtained from purge and trap gas chromatography/mass spectrometry (PT-GC/MS) and purgeable organic chloride (POCl) analysis for measuring volatile chlorinated hydrocarbons (VCH) in water. Distilled water spike and recovery experiments indicate that at concentrations equal to or greater than 1 microgram per liter, recoveries for most VCH by PT-GC/MS and POCl exceeded 80 percent with relative standard deviations of less than 10 percent. Ground water samples collected from a site on Cape Cod, Massachusetts, where a shallow-unconfined aquifer has been contaminated by VCH, also were analyzed. Results from PT-GC/MS and POCl analyses of duplicate sets of ground-water samples were statistically similar and indicated little bias between the two methods. Identical conclusions about the levels and distribution of VCH in the contamination plume were drawn from the two data sets. However, only PT-GC/MS analyses provided information on the individual compounds present in the ground water.

[1] U.S. Geological Survey, WRD, Denver, Colorado
[2] U.S. Geological Survey, WRD, Lawrence, Kansas
[3] Dohrmann Rosemount Analytical Division, Santa Clara, California

EFFECT OF PARTICLE SIZE AND MINERALOGY ON SORPTION OF NONIONIC ORGANIC SOLUTES TO GLACIAL OUTWASH SEDIMENTS, CAPE COD, MASSACHUSETTS

by

Larry B. Barber II[1]

ABSTRACT

Transport of organic contaminants in ground water is influenced by sorption to aquifer sediments. However, the effects of sediment geochemical properties on sorption and transport are poorly understood. In this study, sorption of nonionic organic compounds onto particle size and mineralogical fractions from a glacial outwash aquifer on Cape Cod, Massachusetts, was evaluated. Sediment organic carbon (SOC) and surface area of the aquifer sediments increased with decreasing particle size. Abundance of magnetic minerals also increased with decreasing particle size. SOC and surface area were preferentially associated with magnetic minerals, and the magnetic fraction contained about 80 percent of the SOC in the bulk sediment.

Batch equilibrium-isotherm experiments were conducted using tetrachlorobenzene (TCB), pentachlorobenzene (PCB), and 2,6-di-t-butyl-benzoquinone (DTBB). For a given solute, sorption increased with decreasing particle size (increasing SOC). Within a particle size class, the magnetic fraction had higher SOC and greater sorption than did the bulk or non-magnetic fractions. Although SOC content was typically less than 0.1 percent, sorption was consistent with a partition mechanism. Measured uptake of TCB, PCB, and DTBB was close to that predicted based on their octanol/water partition coefficients. At SOC contents less than 0.01 percent, sorption was slightly greater than predicted. Removal of SOC from the magnetic minerals by hydrogen-peroxide treatment decreased sorption of PCB in proportion to the decrease in SOC (about 50 percent). However, the significant uptake of PCB after SOC removal, and the nonlinearity of the isotherm for the treated minerals indicate that adsorption is contributing to uptake.

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[1] U.S. Geological Survey, WRD, Denver, Colorado

USE OF AZAARENE TRACERS TO EVALUATE FRACTURE FLOW FROM AN IN-SITU OIL-SHALE RETORT, ROCK SPRINGS, WYOMING

by

Larry B. Barber, II[1] and Jerry A. Leenheer[1]

ABSTRACT

Ground-water samples collected from an in-situ oil-shale retort site located near Rock Springs, Wyoming, were analyzed for the presence of azaarene compounds (nitrogen heterocycles) to evaluate whether the contaminants are moving off site. It was hypothesized that if azaarenes are moving through a porous medium, chromatographic separation of compounds with significantly different water solubilities should occur. If transport is through open fractures, chromatographic separation should not occur. Specific conductance, pH, and concentrations of dissolved organic and inorganic carbon also were measured. The azaarene composition of ground water collected from the retort chamber was very complex and more than 100 compounds were detected at concentrations ranging from 5 to greater than 1,000 micrograms per liter. None of the azaarenes present in the retort water were detected in downfield wells. Specific conductance, pH, and concentrations of dissolved organic and inorganic carbon were highly variable, and values ranged from 1,180 to 40,000 microsiemens per centimeter at 25 degrees Celsius for specific conductance, 8.1 to 13.2 for pH, 13 to 4,200 mg/L (milligram per liter) for dissolved organic carbon, and 5 to 4,600 mg/L for dissolved inorganic carbon. Possible explanations for the absence of azaarenes in any wells other than the retort chamber include; (1) the contaminants have not been transported a measurable distance from the retort chamber because of very slow travel times, (2) the azaarenes are removed from the ground water by sorption to the aquifer material, and (3) there is no direct hydrological connection through open fractures between the retort chamber and the wells studied.

[1]. U.S. Geological Survey, WRD, Denver, Colorado

AN INVESTIGATION OF THE TRANSPORT AND MICROBIAL DEGRADATION OF HYDROCARBONS IN THE SUBSURFACE AT A GASOLINE SPILL SITE IN GALLOWAY TOWNSHIP, NEW JERSEY

By Jeffrey M. Fischer, Arthur L. Baehr, and Nicholas P. Smith[1]

ABSTRACT

A unified study of the transport and microbial degradation of hydrocarbons is being conducted at a gasoline spill site in Galloway Township, N.J. Funding for this research, since 1989, has been obtained from the U.S. Geological Survey Toxic Substances Hydrology Program. The composition of unsaturated zone vapors and shallow ground-water quality are being investigated using an areally and vertically intensive monitoring network. Microbial activity is being analyzed in sediment samples. Field experiments are being conducted to determine parameters for mathematical transport models. Laboratory experiments have been conducted to isolate phenomena to rigorously test sub-model hypotheses. The goal of the project is to integrate results of field and laboratory investigations into mathematical models of the transport and fate of hydrocarbons in the subsurface under natural conditions and during site remediation. The findings of the field, laboratory, and modeling investigations are expected to be transferrable to other contaminated sites.

[1] U.S. Geological Survey, West Trenton, N.J.

A METHOD TO ESTIMATE MICROBIAL DEGRADATION RATES FOR HYDROCARBONS BASED ON GAS TRANSPORT IN THE UNSATURATED ZONE AT A GASOLINE SPILL SITE IN GALLOWAY TOWNSHIP, NEW JERSEY

by A.L. Baehr, J.M. Fischer, M.A. Lahvis, R.J. Baker, and N.P. Smith[1]

ABSTRACT

An approach is presented for estimating hydrocarbon microbial degradation rates at a gasoline spill site. The method is based on modeling oxygen and carbon dioxide transport in the unsaturated zone. The distribution of these gases in the unsaturated zone at the Galloway Research Site provides a distinctive site-wide indication of hydrocarbon degradation. Calibration of a mathematical transport model with this data will allow for computation of hydrocarbon degradation rate. Field and laboratory experiments were conducted to determine the soil diffusion coefficient, a parameter required by the transport model. The field experiment was conducted by slowly injecting fluorocarbon tracers into the unsaturated zone and monitoring the resulting diffusive transport. Laboratory experiments were conducted in columns packed with sediment from the Galloway site.

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[1] U.S. Geological Survey, West Trenton, N.J.

GEOCHEMICAL GRADIENTS IN SHALLOW GROUND WATER CAUSED BY THE MICROBIAL DEGRADATION OF HYDROCARBONS AT GALLOWAY TOWNSHIP, NEW JERSEY

Isabelle M. Cozzarelli[1], Mary Jo Baedecker[1] and Jessica A. Hopple[1]

ABSTRACT

A study of the geochemical gradients and alterations in ground water adjacent to a gasoline spill in Galloway Township, N.J., was undertaken to examine the geochemical effects of the microbial degradation of organic contaminants in part of the New Jersey Coastal Plain. A detailed study of the ground-water geochemistry in a vertical section of the aquifer indicates that ground water near the gasoline source was severely affected by the hydrocarbon contaminants and that the vertical changes of geochemical constituents were significant. The concentration of dissolved hydrocarbons, mostly aromatic hydrocarbons, reached a maximum of 33.6 mg/L (milligrams per liter) in anoxic ground water 15.5 ft (feet) below land surface. The highest concentrations of organic acids (1.6 mg/L) are found in this same location (15.5 ft below land surface) where aromatic hydrocarbons were at maximum concentrations throughout the study period (June 1989 through July 1990). The reactions controlling the distribution of hydrocarbons and organic acids are microbially mediated oxidation-reduction reactions. The important degradation reactions in the shallow ground water are nitrate reduction, iron reduction, and sulfate reduction. Below a depth of 18 feet, aerobic degradation and, to a lesser extent, nitrate reduction occur. These reactions cause significant geochemical alterations of the ground-water chemistry and aquifer solids.

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[1] U.S. Geological Survey, 431 National Center, Reston, VA 22092

ABUNDANCE AND DISTRIBUTION OF MICROBIAL GUILDS IN A SUBSURFACE PLUME OF GASOLINE CONTAMINATION AT GALLOWAY TOWNSHIP, NEW JERSEY

By Aaron L. Mills and Susan E. Randall

ABSTRACT

The distribution of total, viable, and hydrocarbon-degrading microorganisms in the sediments and ground waters of a gasoline-contaminated site in Galloway Township, New Jersey, was determined in May and July, 1990. Total bacteria (determined by acridine-orange direct counts) were more uniformly distributed with depth than were the total viable microbes (aerobic plate counts) or the hydrocarbon utilizers (aerobic plate counts or most-probable-number estimates). These organisms were most abundant at the surface of the the soil and near the surface of perched or regional water tables. The presence of microbial assemblies that could grow under anaerobic conditions at the expense of the hydrocarbon and alternative inorganic terminal electron acceptors (NO_3^- or SO_4^{2-}) was consistent with the presence of products of anaerobic microbial respiration in samples from the same sites.

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OVERVIEW OF NONPOINT-SOURCE CONTAMINATION OF THE HIGH PLAINS AQUIFER IN SOUTH-CENTRAL KANSAS

by John O. Helgesen[1], Lloyd E. Stullken[2], and A.T. Rutledge[3]

ABSTRACT

Ground-water quality was assessed in a 5,000-square-mile area of the High Plains aquifer in south-central Kansas that is susceptible to nonpoint-source contamination from agricultural and petroleum-production activities. Of particular interest were agricultural chemicals and oil-derived hydrocarbons associated with brines that formerly were disposed of into unlined ponds. Ground-water sampling sites were randomly selected within discrete land-use areas (irrigated cropland, petroleum-production land containing former brine-disposal ponds, and undeveloped rangeland). The sampling design enabled statistical hypothesis testing of the effects of land use, lithology of the unsaturated zone, and type of well sampled.

Results indicate that water beneath irrigated cropland and petroleum-production land is characterized by significantly (95-percent confidence level) larger concentrations of several inorganic constituents than is water beneath undeveloped rangeland. Nondegraded pesticides and oil-derived hydrocarbons were detected only infrequently in the aquifer. The unsaturated zone above the aquifer contains substantial clay that inhibits the downward movement of water and solutes. The type of well sampled (irrigation wells compared to small-yield wells) apparently is not an important factor in the characterization of water quality beneath the irrigated-cropland areas.

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[1] U.S. Geological Survey, Lawrence, Kansas.

[2] Kansas State Board of Agriculture, Division of Water Resources, Topeka, Kansas.

[3] U.S. Geological Survey, Richmond, Virginia

COMPARISON OF RELATIONS BETWEEN SHALLOW-GROUND-WATER QUALITY AND LAND USE IN TWO NEW JERSEY COASTAL PLAIN AQUIFER SYSTEMS

by Eric F. Vowinkel[1]

ABSTRACT

Relations between shallow-ground-water quality and land use were tested statistically by analysis of data from wells located within the outcrop areas of two aquifer systems in the New Jersey Coastal Plain. Water samples from wells in undeveloped, agricultural, residential, and urban-nonresidential areas were analyzed for nitrate and purgeable organic compounds. Water samples from wells in agricultural areas were analyzed for five pesticide groups: organochlorine, organophosphorous, carbamate, triazine/acetanilide, and chlorophenoxy acid.

In both aquifer systems, similar relations between these constituents and land use were determined. Concentrations of nitrate in ground water beneath agricultural land were significantly higher than those in ground water underlying other land-use areas. Purgeable organic compounds were detected less frequently in ground water beneath agricultural land than in ground water underlying urban or undeveloped land. The detection frequency of each pesticide group was similar for both aquifer systems; carbamate insecticides were detected most frequently.

[1] U.S. Geological Survey, West Trenton, NJ

DISTRIBUTION OF DISSOLVED ATRAZINE AND TWO METABOLITES IN THE UNCONFINED AQUIFER, SOUTHEASTERN DELAWARE

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ABSTRACT

Water from 20 shallow wells in a mostly agricultural watershed in southeastern Delaware was analyzed for atrazine and two of its metabolites, desethylatrazine (DEA) and deisopropylatrazine (DIA), along with nitrate and silica. Atrazine or its metabolites were present in all the water samples and ranged in concentration from a trace to 2,830 nanograms per liter. DEA was the predominant metabolite and in most wells was present in higher concentrations than atrazine. High concentrations of atrazine and metabolites are associated with high concentrations of nitrate. The ratio of DEA to total atrazine increased from less than 0.1 to from 0.8 to 1.0 along a ground-water-flow path originating in an agricultural area. Changes in concentration and relative proportions of atrazine and the metabolites along the flow path might be caused by continued microbial degradation in the ground water, although other processes, such as dilution and changes in aquifer recharge rate, also could be important.

RECONNAISSANCE INVESTIGATIONS OF THE EFFECTS OF IRRIGATION DRAINAGE ON WATER QUALITY, BOTTOM SEDIMENT, AND BIOTA IN THE WESTERN UNITED STATES

Herman R. Feltz[1], Marc A. Sylvester[1], and Richard A. Engberg[2]

In response to concerns expressed by the U.S. Congress and others over contamination at the Kesterson National Wildlife Refuge in California, the U.S. Department of the Interior started a program in 1985 to identify the nature and extent of irrigation-induced water-quality problems that might exist in other areas of the western United States.

An evaluation of the results of completed reconnaissance investigations indicates that selenium is the trace element commonly found at elevated concentrations in water, bottom sediment, and biota, and has the greatest potential to cause toxicological effects in most of the study areas. Impaired bird reproduction and deformed embryos were noticed in 5 of 20 areas studied. Bioaccumulation and biomagnification of selenium is evident in some areas. Elevated concentrations of selenium associated with irrigation drainage can be either localized or widespread.

[1] U.S. Geological Survey, Reston, Va., and Menlo Park, Calif., respectively.

[2] Department of the Interior, Washington, D.C.

SOURCES, SINKS, AND EFFECTS OF SELENIUM AT STEWART LAKE WATERFOWL MANAGEMENT AREA, JENSEN, UTAH

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Bruce Waddell [2]
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ABSTRACT

Soils in the area of Stewart Lake are derived from alluvium and Mancos Shale and contain concentrations of total selenium ranging from 200 to 3,000 parts per billion. Subsurface drains constitute the only source of surface inflow to Stewart Lake. During 1986-89, the median concentration of selenium in water discharging from the drains was 43 micrograms per liter (ug/L) and was associated with drainage from soils developed on Billings Clay. Stewart Lake acts as a sink for selenium discharged by the drains. Median concentrations of selenium discharged by every drain exceeded the standard of 5 ug/L established by the State for the protection of aquatic wildlife, and 98.8 percent of all samples of drainwater exceeded the standard. However, only 25 percent of the daily load of 252 grams of selenium entering the lake discharged to the Green River.

Nineteen percent of waterfowl eggs collected from Stewart Lake contained concentrations of selenium that exceeded 15 micrograms per gram (ug/g), a value associated with deformities in mallard embryos. Several deformed duck embryos were found within the area and concentrations of selenium in livers of a coot and a mallard from Stewart Lake exceeded 19 ug/g, a concentration associated with deformities at Kesterson National Wildlife Refuge in California.

[1] U.S. Geological Survey, Salt Lake City, UT

[2] U.S. Fish and Wildlife Service, Salt Lake City, UT

[3] U.S. Bureau of Reclamation, Salt Lake City, UT

PHYSICAL, CHEMICAL, AND BIOLOGICAL PROCESSES IN WATERS AFFECTED BY ACID MINE DRAINAGE: FROM HEADWATER STREAMS TO DOWNSTREAM RESERVOIRS

Briant A. Kimball[1]

ABSTRACT

Since 1986, the Upper Arkansas River Surface-Water Toxics Project has focused on the geochemistry of metals from acid mine drainage, and on selected aspects of the effects of metals on biological communities. St. Kevin Gulch, near Leadville, Colorado, has been the field site for studying physical, chemical, and biological processes in mountain streams affected by acid mine drainage. Four spatially and temporally intensive sampling efforts in St. Kevin Gulch have tested hypotheses about the process of iron photoreduction, the processes causing metal attenuation dowsntream from acid inflows, the effects of substream flow on metal transport, and the process of phosphorus uptake by algae in iron-rich, acid waters. Other studies have detailed the mineralogy and physical characteristics of hydrous iron oxides to help answer questions about transformations of metals affecting transport in the stream. Biological aspects have included metal uptake by plants, effects of metals on microbiological populations, and pathways for phosphorus uptake by algae. Biological and geochemical aspects of metal transport are combined in the studies of wetland hydrology and metal flux through a wetland at the mouth of St. Kevin Gulch.

Where headwater streams enter the Arkansas River, geochemical processes in mixing zones can transform the metals. Downstream from mixing zones, iron colloids affect the transport of metals over a 250-kilometer reach from Leadville to Pueblo Reservoir. Reservoir sediments that include the colloids and associated metals, represent a temporary endpoint for the metals leaving the Leadville area. Analysis of sediment cores has provided a record of sediment and metal loading from upstream sources.

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[1] U.S. Geological Survey, Salt Lake City, Utah

USE OF MASS-FLOW CALCULATIONS TO IDENTIFY PROCESSES CONTROLLING WATER QUALITY IN A SUBALPINE WETLAND RECEIVING ACID MINE DRAINAGE, ST. KEVIN GULCH, COLORADO

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ABSTRACT

This paper presents preliminary mass-flow calculations for iron, copper, cadmium, zinc, and manganese in surface water flowing through a subalpine wetland affected by acid mine drainage near Leadville, Colorado. Instantaneous mass-flow calculations for June 1, June 20, and July 11, 1988, indicate iron and copper were being removed from surface water by the wetland on the former two dates. Cadmium and zinc were flushed from the wetland on June 1 and exhibited conservative behavior (that is, mass inflow equaled mass outflow) on June 20. Manganese, however, behaved conservatively on June 1 but was flushed from the wetland on June 20. Mass inflows of the five metals were greater than outflows on July 11. These patterns are enhanced by complications in the surface-water hydrology of the wetland at that time and are, therefore, not definitive. Processes causing metal removal by the wetland include the formation and precipitation of iron oxyhydroxide material and the pH-controlled sorption and precipitation of copper.

Use of variation in solute concentration to identify interactions of the substream zone with instream transport

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In St. Kevin Gulch (Upper Arkansas River basin; Leadville, Colo.), a reconnaissance study was conducted to identify hydrochemical interaction of the substream zone with instream transport. Acid mine drainage causes several trace metals to be present at elevated concentrations relative to those typical of pristine Rocky Mountain streams. The reconnaissance was an adjunct to an experimental study of trace-metal retention within the streambed.

In streams that receive acid mine drainage, instream alterations of concentrations of various solutes can occur episodically. The primary experiment included maintenance of steady instream lithium concentration above background level, sharp changes in sodium concentration, and adjustments of pH sufficient to cause variations in copper concentration. Four shallow, open 'wells' in the substream zone adjacent to the stream channel were sampled.

Lithium and sodium concentrations were interpreted to identify a definite, highly variable, hydraulic connection between the substream zone and the stream channel. In this reconnaissance study, copper concentrations varied within the substream zone; however, the variations could not be related to the experimentally induced instream variations. Thus, the coupled hydrochemical interaction of the substream zone with instream solute transport may differ among solutes.

PREDICTIVE MODELING OF COPPER, CADMIUM, AND ZINC PARTITIONING BETWEEN STREAMWATER AND BED SEDIMENT FROM A STREAM RECEIVING ACID-MINE DRAINAGE, ST. KEVIN GULCH, COLORADO

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ABSTRACT

St. Kevin Gulch is a small mountain stream that receives acid-mine drainage from an abandoned mining area. The streamwater carries elevated concentrations of iron, aluminum, copper, cadmium, zinc, and several other elements. The streambed is coated with abundant iron-rich hydrous oxides that appear to attenuate the dissolved metals. This work examines pH-dependent partitioning of copper, cadmium, and zinc between streamwater and bed sediment collected from three sites along St. Kevin Gulch. Observed metal-partitioning behavior is compared with computer-model simulations using a surface-complexation sorption model and the assumption that hydrous iron oxide is the sole sorbent material for metals. Results show that the sorption model is able to predict copper and zinc partitioning, but slightly underestimates cadmium partitioning to the sediment. Partitioning behavior of copper and zinc appears to be dominated by sorption on hydrous iron oxide present in the bed sediment.

PHOSPHATE UPTAKE BY ALGAE IN A STREAM CONTAMINATED BY ACID MINE DRAINAGE, ST. KEVIN GULCH LEADVILLE, COLORADO

By Cathy M. Tate[1], Diane M. McKnight[2], and Sarah A. Spaulding[3]

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ABSTRACT

Low concentrations of phosphorus (P) in Rocky Mountain streams potentially limit algal growth. Factors altering P concentration, such as adsportion of P onto hydrous iron-oxides in streams contaminated by acid mine drainage, can have an important effect on stream biota. An hour-long injection of phosphate ($^{32}PO_4$) containing radioactive phosphorus (^{32}P) into a 175-meter reach of St. Kevin Gulch was used to study pathways by which benthic algae assimilate P for growth in streams contaminated by acid mine drainage. Algae covered 47 percent and hydrous iron-oxides 30 percent of the stream channel during the study. Samples of water, suspended solids, algae and hydrous iron-oxides were collected at five sites (the three upstream sites were shaded and the two downstream sites exposed to sunlight) to follow the pathways of ^{32}P. ^{32}P in samples of water and algae decreased downstream from the injection site, whereas ^{32}P in samples of hydrous iron-oxides indicated no consistent downstream pattern. ^{32}P per milligram dry weight of suspended solids increased greater than twofold in nonshaded compared with shaded sections of the stream channel, which indicates that light altered concentrations of ^{32}P in suspended solids. ^{32}P was greater in algae and adenosine triphosphate extracts of algae than in hydrous iron-oxides which indicates algal uptake of ^{32}P directly from water. Prior to the injection, acid phosphatase activity was measured and was greater during the day than at night, which indicates that algae have a greater demand for P during periods of photosynthesis. ^{32}P per streambed area for algae and hydrous iron-oxides, indicated that both are important sinks for $^{32}PO_4$ in St. Kevin Gulch. Algae can directly remove and assimilate available phosphate from the water for growth and successfully compete with abiotic pathways (adsorption of phosphates onto hydrous iron-oxide) for this limiting nutrient.

TRANSITION METAL GEOCHEMISTRY OF THE UPPER ARKANSAS RIVER, COLORADO

by Edward Callender[1], Briant A. Kimball[2], and Ellen V. Axtmann[3]

ABSTRACT

Whole-water and bottom-sediment samples were collected along the length of the Upper Arkansas river in south-central Colorado in October 1988 and May 1989. Water samples were filtered at several pore sizes and sediment samples were sieved through a 60 micrometer screen. Water samples were analyzed for dissolved and particulate iron, manganese, and zinc whereas sediment samples were analyzed for the same elements contained in an extractable and total sedimentary phase.

During a period of low flow (October), the concentration of dissolved iron appears to be controlled by equilibrium with amorphous-iron phases, and the manganese and zinc partitions to the particulate fraction in the downstream direction. Under high-flow conditions (May), the distribution patterns of all three metals are controlled by physical factors, such as discharge and turbulence.

The downstream attenuation of sedimentary iron, manganese, and zinc follow different patterns. Iron is added to the river sediments by acid-mine drainage near Leadville and there is no increase or sustained partitioning of iron to the sediment downstream. Manganese and zinc are also contributed by contaminant inflows near Leadville but appear to be reacting between the water column and bed sediment in downstream direction. A substantial fraction of these sedimentary metals is present as an easily extractable phase. Iron occurs mostly in the mineral fraction of the bed sediment.

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[1] U.S. Geological Survey, Reston VA
[2] U.S. Geological Survey, Salt Lake City, UT
[3] U.S. Geological Survey, Denver, CO

USE OF A MULTI-LEVEL SAMPLER TO DETERMINE VERTICAL CONCENTRATION GRADIENTS OF VOLATILE AROMATIC HYDROCARBONS IN GROUND WATER, GALLOWAY TOWNSHIP, NEW JERSEY

by Jacob Gibs, G. Allan Brown, and Kenneth S. Turner[1]

ABSTRACT

Observation wells are a standard means for gaining access to ground water in order to determine its chemistry. Evidence indicates that observation wells can produce a biased sample when analyte concentrations are not uniform in the vicinity of the well screen, however. This paper demonstrates that use of a wire-wound screen integrates the water chemistry as a function of depth in ground water contaminated by leaded gasoline at Galloway Township, New Jersey. Two multiport samplers were designed, built, and installed 55 feet apart. The multiport samplers were used to collect seven independent samples within the screened zone to simulate a 5-foot-long, 2.375-inch-outside-diameter conventional wire-wound screen. Samples collected with the two multiport samplers show that a conventional 5-foot-long well screen that integrates contaminant concentrations over its length can result in a contaminant concentration that is as little as 28 percent of the maximum concentration observed in the multiport sampler.

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[1] U.S. Geological Survey, West Trenton, New Jersey

USE OF MATHEMATICAL PROGRAMMING COUPLED WITH A TRANSPORT MODEL TO OPTIMIZE THE DESIGN OF VAPOR-EXTRACTION SYSTEMS

by Claire Welty[1], Arthur L. Baehr[2], Craig J. Joss[1], and Jonathan J. A. Dillow[1]

ABSTRACT

An approach for simulating optimal design of vapor-extraction systems is presented. A three-dimensional, steady-state, air-flow model coupled with an optimization algorithm is being developed to determine optimal pumping rates and placement of venting wells for withdrawing volatile contaminants from soil. Two problems will be solved and results will be compared using the coupled air-flow/optimization code: a flow-maximization problem and a cost-minimization problem. Problem constraints include maximum or minimum total flow rate (and corresponding vacuum) at each well and budgetary constraints.

A second component of this work is development of a three-dimensional, transient, compositional model to simulate subsurface hydrocarbon-vapor transport and microbial degradation. This numerical model will be linked to an optimization algorithm to determine a schedule of air withdrawal/injection rates at the well locations previously found using the air-flow/optimization code. The objective will be to minimize cleanup costs during a specified time period, subject to budgetary constraints and a target subsurface distribution of contaminants in the vapor and (or) the soil. Finally, a new field method for determining air-phase permeabilities is discussed.

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GAS-CHROMATOGRAPHIC METHODS FOR DETERMINING THE COMPOSITION OF THE VAPOR PHASE IN GASOLINE-CONTAMINATED SOILS

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ABSTRACT

A gas chromatograph with flame-ionization and thermal-conductivity detectors is being used to monitor concentrations of hydrocarbons and inorganic gases in unsaturated-zone soil-gas samples. The gas chromatograph is located at the site of an underground gasoline spill in Galloway Township, New Jersey. Inorganic gases are detected by thermal-conductivity-detector analysis and quantified by use of linear-regression standard curves. Hydrocarbons are detected by using flame-ionization-detector analysis, and 16 specific hydrocarbons are identified by their retention times and are quantified by using linear-regression analysis. A method of carbon-number analysis was developed to facilitate semiquantitative evaluation of flame-ionization chromatograms that contained unidentified peaks. Carbon-number analysis involves partitioning chromatograms into retention-time increments and assuming that each increment contains hydrocarbons having the same number of carbon atoms.

[1] U.S. Geological Survey, West Trenton, N.J.

DISTRIBUTION OF ORGANIC AND INORGANIC CONSTITUENTS IN GROUND WATER AT GALLOWAY TOWNSHIP, NEW JERSEY

Mary Jo Baedecker[1], Isabelle Cozzarelli[1], and Curtis Phinney[1]

ABSTRACT

Gasoline from a leaking storage tank on a farm in Galloway Township, New Jersey, resulted in the accumulation of free product in a shallow sand aquifer. Benzene, toluene, and the C_2-alkylbenzenes were the most abundant components of the gasoline, and these compounds were found in a perched-water zone and in the water-table aquifer. Other components of the gasoline, the C_3- and C_4-alkylbenzenes and naphthalenes, were found in the water, and these compounds may remain longer in the aquifer than benzene, toluene, and the C_2-benzenes. The biodegradation of hydrocarbons by aerobic and anaerobic processes results in changes in the distributions of organic compounds and inorganic aqueous species in the perched-water zone and water-table aquifer. Differences in the geochemistry of water from these two water bodies are the result of movement of water and biogeochemical processes.

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[1] U.S. Geological Survey, 431 National Center, Reston, Virginia 22092

NON-FICKIAN VAPOR TRANSPORT IN SAND COLUMNS CONTAMINATED WITH VOLATILE ORGANIC COMPOUNDS

by Clifford J. Bruell[1], Craig D. Gilbert[1], and Arthur L. Baehr[2]

ABSTRACT

The vapor-phase component of a highly volatile organic compound in a porous medium may exceed the constraint of a dilute species diffusing in a bulk phase assumed by Fick's Law. The Stefan-Maxwell equations provide a more general model for quantifying steady-state vapor diffusion of volatile organic substances. Experimental soil-column diffusion data show that a Fickian-based model overestimated soil tortuosity by 35 percent and failed to account for the displacement of atmospheric gases (For example, oxygen) by the diffusing volatile organic compound. Therefore, use of a Fickian-based model can lead to an erroneous interpretation of soil-gas data if depleted oxygen levels are attributed to microbial degradation.

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METHOD FOR THE SYSTEMATIC EVALUATION OF ORGANIC CHEMICAL RETENTION BY SOLID-PHASE-EXTRACTION COLUMNS

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ABSTRACT

A simple method for evaluating the breakthrough of organic chemicals from solid-phase-extraction (SPE) columns is suggested. This method is applicable to a wide range of SPE columns, organic chemicals, solution characteristics, and flow rates. The method employs a six-port injection valve and an air-tight SPE column holder placed between an HPLC pump and detector. A typical frontal chromatography (breakthrough) experiment is conducted. The aqueous mobile phase has the appropriate analyte and solution characteristics (pH, ionic strength, solvent modifier, analyte concentration). Breakthrough of the analyte from the SPE column is monitored in real time by the detector trace. The usefulness and limitations of this method are illustrated with de-isopropyl atrazine, a polar metabolite of atrazine, which is moderately retained by a octadecyl-modified silica gel. The effects of ionic strength, pH, analyte concentration, organic modifier concentration, flow rate, and column size are evaluated.

WET ATMOSPHERIC DEPOSITION OF HERBICIDES IN MINNESOTA

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ABSTRACT

Anthropogenic organic chemicals, including herbicides, can be transported long distances through the atmosphere and deposited in aquatic and terrestrial ecosystems through wet and dry processes. The herbicides, atrazine, alachlor, and cyanazine, have been detected in rain and snow during 1989 and 1990 in St. Paul and Rosemount, Minnesota. Maximum concentrations of atrazine, cyanazine, and alachlor in rain during spring were 1.6, 3.9, and 22 µg/L (micrograms per liter), respectively, but decreased significantly during the following months. During one 24-hour storm in June 1990, 43 sequential samples were collected. Maximum concentration of all three herbicides was present in the first millimeter of rain. Atrazine and alachlor were detected throughout most of the event, but cyanazine was detected in only the first three samples (about 4 mm rain). Yearly fluxes of the three herbicides, alachlor, atrazine, and cyanazine, to the state of Minnesota are estimated to 40, 20, 20 megagrams per year, respectively. Although this is less than one percent of their total agricultural application in Minnesota, the atmospherically deposited atrazine potentially could have a harmful effect on aquatic and terrestrial ecosystems.

RELATIONS BETWEEN WATER DISCHARGE AND HERBICIDE CONCENTRATION IN THE MINNESOTA RIVER, MINNESOTA

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ABSTRACT

The hydrologic and chemical controls on the concentration, sources, and fate of atrazine, alachlor and cyanazine in the Minnesota River are being investigated. The Minnesota River drains a large agricultural watershed (41,500 square kilometers) in south-central Minnesota where application of atrazine, alachlor, and cyanazine is estimated to be 700, 1800, and 550 Mg (megagrams) of active ingredient, respectively. Water samples are collected 3 days a week at Mankato, Minn., and analyzed for atrazine, de-ethyl atrazine, de-isopropyl atrazine, alachlor, de-methylmethoxy alachlor, and cyanazine. The herbicides were isolated by octadecyl solid-phase extraction and analyzed by capillary gas chromatography with a mass-selective detector. Data presented here are for the parent herbicides only (atrazine, alachlor, and cyanazine) for the period spring through autumn 1990. During this time, the herbicide concentrations ranged from less than 30 ng/L (nanograms per liter) to greater than 2,500 ng/L. The presence and variability in concentration of each of the herbicides is interpreted considering hydrologic conditions such as discharge and rainfall and herbicide properties such as application period, water solubility, and environmental half-life. Daily and annual fluxes are calculated for each of the three herbicides in the Minnesota River for 1990. The annual fluxes of these three herbicides account for less than 1 percent of their total application in the watershed.

TRIAZINE HERBICIDES IN SELECTED STREAMS IN ILLINOIS DURING STORM EVENTS, SPRING 1990

by

Richard H. Coupe[1] and Gary P. Johnson[1]

ABSTRACT

A reconnaissance for triazine herbicides in surface waters of the midwestern United States showed that large concentrations of herbicides in surface water can occur following the first runoff event after the application of herbicides to the fields. In the spring of 1990, automatic samplers were installed to collect surface-water samples at three sites in Illinois. The samples were used to quantify the magnitude and duration of the concentration of triazine herbicides during the critical time following the application of herbicides.

A major storm event in mid-May 1990 produced runoff that affected all three sites. Silver Creek near Freeburg had a record peak discharge of 11,000 ft^3/s on May 17 with a recurrence interval of 10 years. The recurrence interval of the event in the Sangamon and the Iroquois Rivers was 10 and less than 2 years, respectively.

In the Silver Creek basin, triazine herbicide concentrations increased sharply during even small events, reaching a peak of 32 µg/L several days before the peak discharge. The Sangamon River demonstrated a different pattern. Concentrations of triazines did not change rapidly and did not reach the levels measured in Silver Creek. The peak concentration of 14 µg/L occurred several days after the peak discharge. The Iroquois River near Chebanse had a peak triazine concentration of 37 µg/L on May 13, 2 days before the peak discharge. On May 19, another storm in the Iroquois River drainage basin produced a peak discharge of 7,300 ft^3/s; the peak triazine concentration associated with this event reached 13 µg/L on the next day.

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DISTRIBUTION OF SELECTED ANTHROPOGENIC ORGANIC COMPOUNDS ON SUSPENDED SEDIMENT IN THE MISSISSIPPI RIVER

by Colleen E. Rostad[1] and Wilfred E. Pereira[2]

ABSTRACT

Transport of organic contaminants on suspended sediment of the Mississippi River was investigated as part of an ongoing, multidisciplinary study. Suspended sediments from 17 sites along the lower and middle Mississippi River, and its major tributaries, were sampled 4 times during 1988 through 1990 at different seasons and river flow conditions. Large-volume (500 liter) water samples collected at each cross section were weighted for water discharge to reflect the river flow at each vertical. Suspended sediments were isolated from the river water samples by continuous-flow, high-speed centrifugation. The samples were then air-dried, extracted, and analyzed for halogenated organic compounds. Selected compounds included chlordane, nonachlor, chlorothalonil, dachthal, hexachlorobenzene, pentachloroanisole, and polychlorinated biphenyls. The concentration on the suspended sediment was converted to nanograms per gram organic carbon. Seasonal fluctuations in river discharge affected the distribution and transport of these compounds in the suspended sediment of the Mississippi River.

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PLANS FOR RESEARCH OF NONPOINT-SOURCE GROUND-WATER CONTAMINATION IN THE COASTAL PLAIN OF THE NORTHEASTERN UNITED STATES

By Anthony S. Navoy[1], Eric F. Vowinkel[1],
Herbert T. Buxton[1] and Paul E. Stackelberg[2]

ABSTRACT

Nonpoint-source ground-water contamination results from the introduction into the recharge process of compounds whose use, existence, or application can be ubiquitous and therefore can affect a wide area. Additionally, the aggregation of many local, individual point sources of contaminants can result in broad areas of contamination. In each of these cases, the definition and management of the source(s) and prediction of the consequences can be difficult without an understanding of the hydrologic processes that affect the movement of contaminants once introduced into ground water.

An investigation is proposed that will examine nonpoint-source ground-water-contamination processes under current conditions in Long Island, New York, and southern New Jersey. The objectives of this investigation are to (1) describe the effects of human activities on regional ground-water quality; (2) investigate the processes affecting the source, integration, and transport of nonpoint-source contaminants in the ground-water system; and (3) develop methods for quantifying and analyzing nonpoint-source ground-water contamination at the local and regional scale.

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Preliminary Analysis of Water-Quality Data from the Shallow, Intermediate, and Deep Zones of Five Land-Use Areas on Long Island, New York

Proceedings report for the U.S. Geological Survey 4th Toxic Substances Hydrology Technical Meeting, March, 1991

By Paul E. Stackelberg and Edward T. Oaksford
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ABSTRACT

Water-quality data obtained from three depth intervals in five areas of differing land use on Long Island, N.Y., were compared to determine whether effects of land use that are observed in the shallow zone can be recognized in deeper parts of the aquifer. The water-quality data consisted of chloride, potassium, nitrate, and total dissolved solids concentrations. The five study areas represent differing degrees of development and are categorized as (1) long-term sewered suburban, (2) recently sewered suburban, (3) unsewered suburban, (4) agricultural, and (5) undeveloped. These study areas lie along the regional ground-water divide, where the predominant direction of ground-water flow is vertically downward.

Median concentrations of the four constituents in the shallow and intermediate depth zones were highest within the agricultural or long-term sewered suburban areas and lowest within the undeveloped area. Median concentrations in the deep zone were typically highest within the long-term sewered suburban area and lowest within the unsewered suburban area. Time-of-travel data indicate that the elevated median concentrations within the deep zone are probably the result of pumping, which accelerates the downward movement of water and its chemical constituents. Comparison of the deep-zone and shallow-zone data among the three suburban areas suggests that the elevated nitrate concentrations in the deep zone of the long-term sewered suburban area reflects historical nitrate-loading patterns, and the elevated nitrate concentrations in the shallow zone of the unsewered suburban area reflects current nitrate-loading patterns.

Results indicate that, in areas where the predominant flow direction is vertical, water-quality patterns observed in shallow parts of the aquifer system tend to be reflected at depth.

INVESTIGATION OF WATER QUALITY, BOTTOM SEDIMENT, AND BIOTA ASSOCIATED WITH IRRIGATION DRAINAGE FROM THE ANGOSTURA RECLAMATION UNIT AREA, SOUTHWESTERN SOUTH DAKOTA, 1988

By Earl A. Greene[1]

ABSTRACT

Water, bottom sediment, and biota were sampled during 1988 within the Angostura Reclamation Unit and adjacent areas in southwestern South Dakota. The study was conducted to determine the concentrations of major ions, selected trace elements, and pesticides in water, bottom sediment, and biota, and to compare the analytical results to various guidelines for environmental protection and to available baseline information.

Concentrations of trace elements in water delivered to Angostura Reservoir appeared to be similar to irrigation drainage water conveyed in return-flow drains, and in the Cheyenne River downstream of the irrigated lands. In general, the study showed that toxicity from selenium or other trace elements and pesticides in water probably is not a persistent problem within the study area or downstream from irrigation return flows.

Trace-element concentrations in bottom sediment were similar to the geochemical baselines for soils of the western United States. Pesticide concentrations in all samples of bottom sediment were less than laboratory analytical reporting limits.

With few exceptions, concentrations of elements and pesticides in biota generally were less than values known to produce harmful effects on growth or reproduction. Selenium concentrations in the majority of whole-body fish tissue samples were greater than baseline values. Several other elements were present in biota at concentrations that were potentially elevated in comparison to baseline values, but concentrations of elements were not unusually high at any sites and no organisms were present in unusually large numbers.

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[1] U.S. Geological Survey

USE OF ENVIRONMENTAL VARIABLES TO ESTIMATE METAL LOADS IN STREAMS, UPPER ARKANSAS RIVER BASIN, COLORADO

By Gregory A. Wetherbee[1] and Briant A. Kimball[2]

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ABSTRACT

Knowledge of processes controlling metal loads aids in the estimation of metal loads at streamflow-gaging stations as well as the abatement of metal contamination in streams. Stream discharge commonly is used as an estimator of loads of conservative constituents, but metals are reactive and affected by many factors in addition to discharge. Numerous hydraulic, chemical, physical, and biological processes contribute to the variability of metal loads in streams. Environmental variables including discharge, pH, alkalinity, total-organic-carbon concentration, sulfate concentration, iron-colloid concentration, and temperature were used in multiple-linear-regression models to estimate total iron, manganese, zinc, cadmium, and calcium loads in the headwaters of the upper Arkansas River. Data from two sampling locations on tributaries affected by mine drainage and two sampling locations on the mainstem of the Arkansas River were analyzed. The concentration of iron colloids described a significant amount of the variation in total iron, manganese, zinc, and cadmium loads at three of the four sampling locations, and seasonal variation in the significance of colloid concentration was indicated. No two models for predicting metal loads were identical, indicating that local variations in water chemistry and environmental processes affect metal loads. Although no unique and transferable combination of processes control metal loads, discharge and iron-colloid concentration are important.

COMPARISON OF RATES HYDROLOGIC AND CHEMICAL PROCESSES IN A STREAM AFFECTED BY ACID MINE DRAINAGE

Briant A. Kimball[1], Robert E. Broshears[2], Kenneth E. Bencala[3], and Diane M. McKnight[2]

ABSTRACT

An in-stream experiment in St. Kevin Gulch near Leadville, Colorado, in August, 1986, examined the interplay between the rate of hydrologic transport and the rates of chemical reactions in affecting streamwater metal concentrations. Lithium chloride was used as a conservative chemical tracer for determining discharge and time of travel along a 1,800-meter reach. With this hydrologic background, a synoptic sampling indicated that reactive and conservative transport of metals occurred downstream from inflows of acidic, metal-rich drainage. There were three basic patterns of mass flow along the reach. Sodium mass flow increased from metal-rich inflows near abandoned mine tailings, and then remained relatively constant. Aluminum and manganese were typically conserved within the stream, with possible mass losses immediately downstream from neutral-pH inflows. Iron was reactive and was removed from the stream water along the entire reach.

Downstream profiles of metals were simulated using a steady-state equation that accounts for longitudinal advection and additions of lateral inflows. These simulations accounted for the removal of iron by introducing a first-order reaction to the steady-state equation. The rate constant for the net in-stream removal of iron was found from calibrating the simulation to the observed iron profile. This net rate represents several processes and not a specific reaction. The combination of mass-balance calculations and solute-transport simulations provides insight to the relative importance of hydrologic and non-hydrologic (chemical and biological) processes that affect metal concentrations in acid mine drainage.

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1. U.S. Geological Survey, Salt Lake City, Utah
2. U.S. Geological Survey, Denver, Colo.
3. U.S. Geological Survey, Menlo Park, Calif.

Preliminary investigation of the effect of hillslope hydrology on the mechanics of solute exchange between streams and subsurface gravel zones

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ABSTRACT

The mechanics of solute transport and retention are being investigated in two gravel-bed streams (Little Lost Man Creek, California and St. Kevin Gulch, Colorado). The overall goal is to determine the influence of hillslope hydrology on solute exchange between the stream channel zone and interstitial water of subsurface gravel zones adjacent to the stream. The first objective of the research was to determine the mechanism responsible for solute exchange between stream and subsurface zones. Solute tracers were released in the stream and in the subsurface, and concentrations were monitored at selected locations to describe transport. Subsurface hydraulic gradients parallel to the stream were measured simultaneously. Observations indicated that the mechanism of solute exchange was advective exchange between the stream and groundwater of the adjacent gravel zone. The stream tracer (chloride) moved away from the stream and entered the subsurface zone where the subsurface hydraulic gradient was away from the stream. The subsurface tracer (bromide) moved toward the stream where the gradient was toward the stream.

The second objective of the research was to examine hydrological controls on advective solute exchange with the subsurface. The magnitude of subsurface hydraulic gradients was observed to vary on a diel cycle. Where the gradient was away from the stream, advection away from the stream increased during the day and decreased at night. Conversely, where the gradient was toward the stream, advection toward the stream decreased during the day and increased at night. As a result, there was more loss of stream water to the adjacent subsurface during the day than at night.

Several possible mechanisms were considered to explain the diel variation in subsurface hydraulic gradients and advection perpendicular to the stream. Evapotranspirative pumping of subsurface water out of the gravel and soil zone at the base of the hillslope was the explanation most consistent with observations. These preliminary findings suggest that hillslope hydrology has important effects on the direction and magnitude of water and solute exchange between streams and subsurface zones. Further investigations of hillslope-stream interactions and effects on solute transport are warranted.

CHEMICAL COMPOSITION OF THE WETLAND VEGETATION RECEIVING THE ACID MINE-DRAINAGE WATERS OF ST. KEVIN GULCH, LEADVILLE, COLORADO

By

B.M. Erickson*, P.H. Briggs*, K.R. Kennedy*,
and T.R. Peacock*

ABSTRACT

Samples of two species of Carex (sedge) were collected from two ecosystems throughout the St. Kevin Gulch wetland, Leadville, Colorado, to evaluate the effect of these acid mine-drainage waters on the vegetation. Summary statistics indicate very little difference between the chemical composition of the two species. The greatest percentage of variance for most elements in one of the species appears to be related to the geographical difference between the 400-m- (meter) square sampling sites and the 100-m-square sampling sites. Clusters of elevated concentrations for 13 elements in the sedge samples were found at the area of first contact with the wetland, indicating that the vegetation has been affected. Clusters of elevated concentrations in other areas of the wetland demonstrated that water from St. Kevin Gulch is not the only source of contamination to the wetland.

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Effect of Organic Matter Coprecipitation and Sorption with Hydrous Iron Oxides on Electrophoretic Mobility of Particles in Acid–Mine Drainage.

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Donald L. Macalady[3], and Terry F. Rees[4].

ABSTRACT

St. Kevin Gulch is a small, acidic ($pH < 4.5$) subalpine stream located near Leadville, Colorado. Hydrous iron oxides (HIO) are dominant minerals in this system. This paper investigates the role of organic matter in controlling the surface charge of HIO formed in St. Kevin Gulch and in laboratory experiments designed to simulate the stream. The electrophoretic mobility (EM) of the iron–rich suspended sediments is strongly related to their organic carbon content and the dissolved organic–carbon (DOC) concentration of the streamwater. Organic–carbon concentration is high (10–24 percent) in the suspended sediments. Concentrations of organic carbon in the suspended sediments and DOC in the streamwater become elevated during spring runoff coincident with the presence of negatively charged suspended sediments. Particles are positively charged during midsummer when concentrations of DOC and organic carbon in the suspended sediments are lowest. This is likely the result of an insufficency of organic matter needed to coat completely the abundant HIO surfaces formed at that time. Organic matter is associated with the suspended sediments as a result of sorption and coprecipitation with HIO. Laboratory experiments with synthetic HIO and Suwannee River fulvic acid indicate coprecipitation removes greater amounts of organic matter than does sorption. However, coprecipitated organic matter has less effect on EM than does sorbed organic matter. Experiments with Suwannee River fulvic acid, Shingle Mill Gulch fulvic acid, and Shingle Mill Gulch whole organic indicated Suwannee River fulvic acid had a much greater effect on EM than either of the Shingle Mill Gulch organic matters, possibly because of differences between the environments from which these samples were isolated.

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Particulate and Colloidal Organic Material and Associated Trace Metals in Pueblo Reservoir, Colorado

Diane M. McKnight[1], James F. Ranville[1] and Richard A. Harnish[1]

The chemical characteristics of particulate organic carbon (POC) in Pueblo Reservoir, Colorado were examined. The Arkansas River is the major inflow to this reservoir. Four POC fractions were isolated by sedimentation, cross flow-ultrafiltration, and centrifugation. A silt fraction, two organic colloid fractions and a mineral colloid fraction were obtained. The silt comprised 56.1 percent of the sediment mass and included intact planktonic diatoms, whereas the organic colloid fraction comprised 13.7 percent of sediment mass, 40 percent of the organic carbon, 60 percent of the organic nitrogen, and 61 percent of the lipid content. The carbon-13, nuclear magnetic resonance spectrum for the organic colloid showed enrichment in carbohydrates and depletion in aromatic moieties. These results indicate that algal material may be the dominant source of the organic colloidal fractions. Iron, manganese, and zinc were enriched in the organic and mineral colloids, demonstrating the importance of these fractions in transport of trace elements.

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BENTHIC INSECTS AS INDICATORS OF LARGE-SCALE TRACE METAL CONTAMINATION IN THE CLARK FORK RIVER, MONTANA

Daniel J. Cain[1] and Samuel N. Luoma[1]

ABSTRACT

The Clark Fork River in western Montana has been contaminated with metals by mining in its headwaters over the past 125 years. Metals originally discharged into the river from an upstream source(s) now contaminate bed sediments 550 km downriver. Metal contamination in the benthic invertebrate community was evaluated over a 381 km (kilometer) reach of the upper river. Six benthic insect taxa, including two caddisflies (Trichopteran) and four stoneflies (Plecoptera), were selected for study. Distributions of these taxa differed within the river and only one taxon, Hydropsyche spp., was collected at all stations. Whole-body metal concentrations in all six taxa from the Clark Fork were elevated relative to specimens collected from uncontaminated tributaries. Contamination patterns, however, varied among taxa and metals. Spatial trends in metal concentrations in two closely related caddisflies, Hydropsyche spp. and Arctopsyche grandis, correlated ($p<0.05$) with the downriver decrease in metal concentrations in the sediments, although within the same station, the absolute metal concentrations in Hydropsyche spp. were approximately 2 times greater than in Arctopsyche grandis. Downriver decreases in the concentrations of some metals also were evident in plecopterans; however, metal concentrations in these animals generally were not significantly correlated with sediment metal concentrations. Differences in metal concentrations among taxa were largely explained by differences in feeding habit. Metal concentrations were higher and showed a stronger relation to sediment metal concentrations in omniverous filter feeders and detritavores than in predators. The results clearly established the presence of metal contamination in benthic invertebrates throughout the 381-km study reach.

[1] U.S. Geological Survey, Menlo Park, CA

THE GLOBE, ARIZONA, RESEARCH SITE--CONTAMINANTS RELATED TO COPPER MINING IN A HYDROLOGICALLY INTEGRATED ENVIRONMENT

By James H. Eychaner[1]

ABSTRACT

Water moving from an area of copper mining has contaminated an arid-zone aquifer and perennial stream near Globe, Arizona, where traveltimes from precipitation to outflow are less than 15 years for ground-water paths entirely within unconsolidated alluvium. During dry climatic cycles, stream channels are ephemeral upstream from the perennial reach, but in wet cycles the aquifer fills and streamflow is continuous throughout the basin.

The most contaminated water contains more than 1,000 mg/L (milligrams per liter) of iron and sulfate and 100 mg/L of aluminum and copper. A front at which pH falls below 5 has advanced through the alluvium at a rate of 0.2 to 0.3 kilometers per year during the past several decades and could arrive at the perennial reach within 6 to 8 years. Dissolved manganese concentrations in streamflow increased from 0.5 mg/L in 1979 to about 35 mg/L in 1988-89. At one streamflow station, dissolved nickel began to increase in 1988 and alkalinity began to decrease in 1989, but no change has been measured at another station 5 kilometers downstream. Aquifer cleanup began in 1987, but several years will pass before its success can be assured.

In the ground water, pH is controlled by reactions with carbonate minerals, by slower reactions with silicate minerals, and by production of hydrogen ions in metal-oxidation reactions. Dispersed gypsum crystals, iron-oxide coatings, and silicate minerals altered to clays are found in well cuttings from contaminated alluvium. In a mass-transport model of the advancing plume, calcite, dolomite, microcline, and manganese oxide dissolved from the aquifer, and ferric hydroxide, gypsum, and gibbsite precipitated. Manganese oxide in uncontaminated alluvium is an effective oxidant of ferric iron, but in column experiments about 7 moles of iron precipitated for each mole of manganese that dissolved; identification of the dominant terminal electron acceptors is uncertain.

As the ground water becomes perennial streamflow, gas exchange with the atmosphere causes carbon dioxide to decrease and oxygen to increase; manganese oxide minerals form on the streambed. About 0.9 mole of calcium dissolved from calcite for each mole of manganese that precipitated in a reaction-path model.

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[1] U.S. Geological Survey, Tucson, Arizona

PARTICLE-TRACKING ANALYSIS OF FLOW IN THE STREAM-AQUIFER SYSTEM IN PINAL CREEK BASIN, ARIZONA.

by James G. Brown
U.S. Geological Survey

ABSTRACT

Acidic water has contaminated a stream-aquifer system near Globe, Arizona. A plume of contaminated ground water in alluvium and shallow basin fill along Miami Wash and Pinal Creek comes in part from an acidic lake that was drained in 1988. Simulated traveltimes from Webster Lake through the alluvium to Inspiration Dam were less than 15 years. However, simulated traveltime from this lake to a well perforated in shallow basin fill exceeded 400 years. Inadequate simulation of individual pathlines in some areas may be the result of discretization effects, the use of inaccurate aquifer properties to represent basin fill, water-level flucuations that result in downward movement of water, and (or) contaminants in the shallow basin fill that are present as a result of dispersive flow (which was not accounted for in the present analysis). Tritium concentrations indicate that water in the most contaminated part of the plume may be less than 20 years old.

TWO GEOCHEMICAL MASS TRANSPORT CODES: PHREEQM AND MST1D THEIR USE AND LIMITATIONS AT THE PINAL CREEK TOXIC-WASTE SITE.

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ABSTRACT

The chemical evolution of acidic contaminated water at the Pinal Creek toxic-waste site can not be realistically simulated by current contaminant-transport computer codes. The Pinal Creek site serves as an example of the capabilities and limitatations of PHREEQM and MST1D, two computer codes capable of simulating the transport of contaminants affected by aqueous-speciation and mineral dissolution/precipitation processes as well as by the physical processes of advection and dispersion. The results of the PHREEQM and MST1D simulations are remarkably similar, given the difference in their numerical algorithms.

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[3] U.S. Geological Survey, Denver, Colo.

TRACE-ELEMENT TRENDS AT PINAL CREEK, ARIZONA

By Lynda M. Faires[1] and James H. Eychaner[2]

ABSTRACT

Trace-element concentrations vary temporally and spatially in Pinal Creek streamflow. Chemical analysis by inductively coupled plasma - atomic emission spectroscopy (ICP-AES) during 1979-89 revealed temporal trends of increasing concentrations for dissolved manganese and nickel. Spatial trends were examined by collecting samples from streamflow and shallow ground water at 11 sites in a 6-kilometer perennial-flow reach during March 1990. Spatial trend evaluation for seven trace elements (barium, cadmium, cobalt, copper, molybdenum, nickel, and zinc) was made possible through the use of inductively coupled plasma - mass spectrometry (ICP-MS), which provides detection limits one to two orders of magnitude below those of ICP-AES.

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[2] U.S. Geological Survey, Tucson, AZ

ISOLATION OF MULTIPLE CLASSES OF PESTICIDES FROM LARGE-VOLUME WATER SAMPLES USING SOLID PHASE EXTRACTION CARTRIDGES

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ABSTRACT

A solid-sorbent sampling method that provides for the trace enrichment of multiple chemical classes of organic pesticides is described. High-capacity solid-phase extraction cartridges containing 10 grams of octadecylsilyl-bonded porous silica were evaluated for their ability to preconcentrate 38 pesticides spiked into 10 L (Liters) of distilled water. Single cartridge collection efficiencies were very good for nearly all pesticides evaluated, except for dimethoate, a polar, highly water-soluble compound. Retention of analytes by the front cartridge alone accounted for an average 71 to 102 percent recovery of the total mass of analyte spiked for all but three analytes. For studies in which low sample flow rates of 20 to 35 milliliters per minute can be used to extract 10 L of water, high-capacity solid phase extraction appears suitable for the isolation and preconcentration of a variety of pesticide classes.

CALCULATION OF CONSERVATIVE-TRACER AND FLUME-DISCHARGE MEASUREMENTS ON A SMALL MOUNTAIN STREAM.

By Gary W. Zellweger, USGS, Menlo Park
and Wendy S. Maura USGS, Denver

ABSTRACT

An experiment was conducted to (1) determine which sections of a reach of a stream were losing water (2) test if a sequence of three simultaneous lithium-tracer injections spaced along the 231-meter reach could detect the loss, and (3) compare discharge measurements from three 3-inch Parshall flumes with discharge calculations from the tracer-dilution method. Results indicate that about 2 liters per second, approximately 20 percent of the discharge, was being lost in the lower half of the study reach. The multiple tracer-injection method was able to detect the loss and to determine where in the reach the loss was occurring. Flume-discharge measurements also indicate the loss but did not agree with the tracer-dilution-discharge measurements at all sites.

CHEMICAL MODELING OF ACID MINE WATERS IN THE WESTERN U. S.

Darrell Kirk Nordstrom[1]

ABSTRACT

Both inverse and forward chemical modeling can be applied to the interpretation of mine waste contamination problems with some success. Forward modeling has been used at Iron Mountain, California to simulate an acid mine water of pH 0.46 based on inverse modeling results. Modeling of such concentrated acid mine waters raises serious difficulties with pH measurements, charge imbalance calculations and non-ideality corrections during speciation calculations. Calculations of saturation indices for acid mine waters commonly show saturation to supersaturation with respect to ferrihydrite, gibbsite and barite and reflect a solubility control by these minerals. These results have increased our understanding of some of the major processes operating both during the production and the downstream attenuation of acidity and metals in acid mine waters.

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A NEW METHOD FOR DETERMINING SOIL MACROPOROSITY

by

R. W. Healy[1], G. M. Reimer[2], J. M. Been[2], and S. L. Szarzi[2]

ABSTRACT

Results of air-permeability and gas-tracer tests, along with measurements of air-filled porosity can be used to develop models of continuous pore space within soils. These models can then provide a convenient framework for studying the spatial and temporal variability of macropores in the field as well as provide insight to water and solute movement through macroporous soils.

Air-permeability and gas-tracer tests were conducted in the laboratory on uniformly packed columns of silica sand and silt loam. A dilute mixture of helium and air was used as the tracer gas. Simulated macropores were constructed from stainless-steel tubes and were inserted into the columns. Results of tests were noticeably affected by the presence or absence of macropores. Permeability of the soils was slightly increased by the presence of the macropores. In terms of tracer-test results, breakthrough curves for soils that contained macropores had two concentration peaks. The first peak occurred quickly following tracer injection. The second peak was similar in magnitude and timing to the single peak obtained in tests from the same soil in the absence of any macropores.

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CHLOROFLUOROMETHANES (CCl_3F AND CCl_2F_2): USE AS AN AGE-DATING TOOL AND HYDROLOGIC TRACER IN SHALLOW GROUND-WATER SYSTEMS

Eurybiades Busenberg[1] and L. Niel Plummer[1]

ABSTRACT

Procedures have been developed for sampling ground water for trace levels of chlorofluorocarbons (CFC's, Freons[2]). Samples are collected and stored in 50 milliliter borosilicate glass ampules which are welded at the well site in an environment isolated from air and free from CFC's. CFC concentrations, which remain stable in the sealed ampules for many months, are determined using purge-and-trap gas chromatography with an electron-capture detector to less than 1 picogram per kilogram. The analytical procedures are relatively simple, inexpensive, and require about 10 minutes per sample.

The procedure was applied to shallow quaternary alluvium and terrace deposits in central Oklahoma. Results of about 400 determinations show that CFC's are generally consistent with tritium data and can be extremely useful tracers and age-dating tools in hydrologic studies. Preliminary CFC-model age dating indicates that, in the past 40 years, there may have been two major periods of significant ground-water recharge in central Oklahoma. The first significant period of recharge occurred in the years 1945-60, and the second in 1967-75. The results indicate that much less recharge may have occurred in the drought years 1960-67. Precipitation and tritium results are consistent with this conclusion derived from the CFC's CCl_3F (F-11) and CCl_2F_2 (F-12) model age dating. The precipitation record indicates that another period of significant recharge may have occurred in the mid-1980's that was not recognized in the CFC dating of ground waters. This water may reside in the unsaturated zone or may have not yet intercepted the well-screens of domestic and municipal wells completed in the alluvium and terrace deposits.

Several areas of ground water with F-11 and/or F-12 concentrations in excess of that in equilibrium with modern air have been identified in the alluvial and terrace deposits of central Oklahoma. One area originates within the Oklahoma City limits and extends for several kilometers along the North Canadian River. Another major area originates south-east of the City of Norman and extends more than 20 kilometers along the Canadian River. There may be some correlation between these observed CFC anomalies, high population densities, the geographical location of sewage disposal ponds, and sewage returns into rivers and streams. It is conceivable that some of the CFC contamination may result from the seepage of sewage water with high concentrations of CFC's into the alluvium and terrace deposits.

The preliminary results from the shallow unconfined ground waters in pleistocene sands of the Delmarva Peninsula indicate that there is very little contamination of the shallow aquifers with CFC's. Contamination levels in central Oklahoma are significantly greater than those observed on the Delmarva Peninsula. Model CFC ages for waters from Fairmount, Delaware, also appear to be consistent with tritium results.

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[1] U.S. Geological Survey, Reston, Va.

[2] The use of product or firm names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

The Role of Bed Sediments and Drift in the Transport and Fate of Metallo-Organic Compounds in the Calcasieu Estuary, Louisiana

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ABSTRACT

This paper reports the progress of an on-going study of the relation in riverine and estuarine environments between metals and organic matter with respect to the transport of metals. In this study, supercritical fluids were used to fractionate organic compounds and metallo-organic complexes from bottom sediment and drift from the Calcasieu River Estuary. Bottom sediment, interstitial water, and algal drift samples were collected from sites in a tributary of the Calcasieu River, Louisiana, that receives industrial effluent. The samples were analyzed for heavy metals, including copper, chromium and lead. Concentrations of metals in interstitial water did not correlate with total metal concentrations in the sediment. Concentrations of heavy metals in the drift were as much as two orders of magnitude larger than in the bottom sediment. When supercritical carbon dioxide and carbon dioxide plus methanol as a modifier were used to fractionate the organic matter in the drift the amounts of heavy metals that were recovered in the extracts differed among the metals. Infrared and ultraviolet spectroscopy have been used to identify the functional groups with which individual metals are complexed.

SIGNIFICANCE OF DRIFT AND ORGANIC AND NONORGANIC DETRITUS ON THE MOVEMENT OF SYNTHETIC ORGANIC COMPOUNDS INTO BAYOU D'INDE, LOUISIANA

by Charles R. Demas and Dennis K. Demcheck[1]

ABSTRACT

In 1985, the U.S. Geological Survey began a study of the fate and movement of organic contaminants in the lower Calcasieu River estuary. The estuary, located in southwestern Louisiana, has been heavily affected by numerous chemical industries located along its banks and the banks of its tributaries. The study documented the presence of synthetic organic compounds in the sediments (both bottom and suspended), water, and aquatic organisms in the lower Calcasieu River and one of its tributaries, Bayou d'Inde.

Origins of large concentrations of synthetic organic compounds, especially hexachlorobenzene and hexachlorobutadiene, detected in the bottom material of Bayou d'Inde could not be explained solely by analyses of water and dewatered suspended sediments from Bayou d'Inde. Analyses of drift material, including organic and nonorganic detritus, collected from an industrial outfall canal that empties into Bayou d'Inde showed high concentrations, in the milligrams per kilogram range of these synthetic organic compounds. Field observations indicated that the drift and organic and nonorganic detritus did resettle onto the bottom material which provides a possible explanation for the high concentrations of the compounds. The results indicate that drift and organic and nonorganic detritus, including plant matter and bottom material associated with it, is an important medium for the transport of synthetic organic compounds out of the outfall canal and into Bayou d'Inde.

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[1] U.S. Geological Survey, Baton Rouge, Louisiana

MIGRATION OF ORGANIC COMPOUNDS THROUGH BED SEDIMENTS NEAR AN INDUSTRIAL OUTFALL IN THE CALCASIEU RIVER ESTUARY, LOUISIANA

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Studies conducted in the vicinity of an industrial outfall near the Calcasieu River estuary have shown that the area has been severely affected by the industrial outfall. Water and sediment samples collected above and below the industrial outfall and at the outfall canal have been shown to be contaminated with a variety of chlorinated, brominated, and mixed chlorinated and brominated benzenes, butadienes, biphenyls, diphenyl ethers, styrenes, dihydronaphthalenes, and phenols. Concentration of analytes in the water samples varied from nondetectible to 6 ppb (parts per billion), and the sediment samples varied from nondetectible to 25 ppm (parts per million) (dry weight).

Core samples were collected at the outfall and analyzed, to study the transport and fate of organic compounds as they migrate through bed sediments. After fractionation into 4 cm lengths, the samples were extracted with sonic disruption and analyzed by gas chromatography/mass spectrometry

EFFECT OF THE UNSATURATED ZONE ON THE MIGRATION AND RETARDATION OF A CONSERVATIVE TRACER AT THE PLAINS, GEORGIA, RESEARCH SITE

D.W. Hicks[1], J.B. McConnell[1] and R.K. Hubbard[2]

ABSTRACT

A study was conducted in a farming area near Plains, Georgia, as part of a larger research endeavor by the U.S. Geological Survey; U.S. Department of Agriculture, Agricultural Research Service; and U.S. Environmental Protection Agency that will evaluate the transport and fate of agricultural chemicals in the surface and subsurface environments. The study relied on data collected at a 2-acre research plot (planting area) to define and evaluate the factors that control the transport and fate of conventionally applied agrichemicals. It was hypothesized that the heterogeneity in hydraulic conductivity of the unsaturated zone has a substantial effect on the rates of infiltration and in the transport pathways of solute.

The results of the investigation suggest that the lateral transport of a conservative tracer (potassium bromide solute) may be a substantial component of its dispersion in the unsaturated zone. Data from this investigation indicate that soil heterogeneity substantially affects the migration rates and pathways of surface-applied chemicals, and that one-dimensional (vertical) transport in the unsaturated zone is rare and may be observed only where the soil column is homogeneous and permeable. The lateral migration of solute at the interface between permeable and less permeable material may account for a large part of the dispersion of agrichemicals in the unsaturated zone. Moreover, the lateral rate of movement may be greater than that observed in the vertical.

At the study site, atrazine, alachlor, carbofuran, and the conservative tracer were uniformly applied over the planting area in June 1989, and since application, more than 4,000 soil samples were collected for chemical analysis to evaluate the rates of degradation and transport. Analytical results indicate that during the first 70 days after application, the center of mass of bromide migrated to a depth of about 48 in. (inches) in the planting area. From 70 to 350 days, the migration rate of the bromide mass was retarded at a depth of about 54 in. in the northeastern part of the area, but the tracer continued to migrate vertically to a depth of about 114 in. in the southwestern part of the area. In addition, the total bromide mass in the soil column progressively decreased over time in the northeast and increased in the southwest, indicating that the bromide mass within the planting area was migrating laterally from the upslope area.

The apparent anomalies in the migration of the bromide tracer are directly related to characteristics of hydrogeology in the planting area. The northeastern (upslope) part of the planting area is characterized by a shallow, 8-foot-thick layer of clay having an average vertical hydraulic conductivity of 0.36 ft/d (feet per day). The upper part of the clay layer is extremely dense at a depth of about 48 to 60 in., and in laboratory infiltration tests, would not allow water to pass. Downslope, in the southwestern part of the area, the unsaturated zone is characterized by clean, quartz sand and a higher vertical hydraulic conductivity (1.02 to 5.03 ft/d). Between the northeastern and southwestern parts of the planting area is a transition zone having intermediate lithologies and vertical hydraulic conductivities.

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[1] U.S. Geological Survey, Doraville, Georgia

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APPLICATION OF THE GLEAMS MODEL AT THE PLAINS, GEORGIA, AGRICULTURAL-MANAGEMENT SITE

R. A. Leonard, W. G. Knisel, F. M. Davis, and C. C. Truman[1]

ABSTRACT

In 1988, the U.S. Geological Survey; the U.S. Department of Agriculture (USDA), Agricultural Research Service; the U.S. Environmental Protection Agency, and the University of Georgia began a cooperative study of chemical transport in a representative agricultural management system near Plains, Georgia. A major objective was to establish data bases for interagency model testing and evaluation. The USDA team of the Southeast Watershed Research Laboratory, Tifton, Georgia, through development and testing of the GLEAMS (Groundwater Loading Effects of Agricultural Management Systems) model, is providing a tool specifically aimed at questions associated with soil, management, and climatic variables in the root zone. The GLEAMS model was successfully tested with the limited data currently available and the model applied to a number of practical questions.

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[1] Soil Scientist, U.S. Department of Agriculture, Agricultural Research Service (USDA-ARS); Senior Visiting Research Scientist, Department of Agricultural Engineering; Computer Specialist, USDA-ARS; and Soil Scientist, USDA-ARS, Tifton, GA 31793.

Preliminary Results of a Pesticide Leaching Study at Plains, Georgia

Charles N. Smith[1] and Rudolph S. Parrish[2]

ABSTRACT

A comprehensive field database is being developed for testing various chemical-transport models of pesticide leaching. Three federal agencies (U. S. Environmental Protection Agency, U. S. Department of Agriculture, U. S. Geological Survey) and the University of Georgia Agricultural Experiment Station established a joint research team to investigate and model pesticide movement in a conventionally tilled corn field in the coastal plain of Georgia. The experimental study design, the monitoring procedures for unsaturated and saturated soil zones, and the data-collection methods are presented in the context of a quantitative statistical model testing strategy. Compounds under study include carbofuran (2,3 dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate), atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5 triazine), alachlor (2-chloro-2'6'-diethyl-N-(methoxymethyl)-acetanilide), and a bromide tracer. Initial application losses were about 15 to 39 percent. Of the three pesticides, only carbofuran persisted for 4 months and moved to levels as deep as 3 meters. Half-lives were estimated for all compounds on the basis of total mass in the soil profile.

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MICROBIAL URANIUM REDUCTION

by

Lovley, D. R.[1], Phillips, E. J. P.[1], Gorby, Y. A.[1], and Landa, E. R.[1]

ABSTRACT

The Fe(III)-reducing microorganisms, GS-15, and *Shewanella putrefaciens*, were found to obtain energy for growth by coupling the oxidation of various electron donors to the oxidized form of uranium, U(VI), to the reduced form, U(IV). Both organisms grew in high concentrations (10 millimolar) of dissolved U(VI), but also reduced U(VI) to very low concentrations (< 0.4 micromolar). Studies on the stoichiometry of acetate uptake, metabolism of [2^{14}C]-acetate, and U(VI) reduction indicated that GS-15 oxidized acetate to carbon dioxide with U(VI) as the sole electron acceptor. Hydrogen, formate, lactate, and pyruvate could serve as electron donors for U(VI) reduction by *S. putrefaciens*. *Desulfovibrio desulfuricans* also rapidly reduced U(VI) to U(IV) but could not obtain energy to support growth from this reaction. Microbial U(VI) reduction in defined media and aquatic sediments was much faster than commonly cited abiological mechanisms for U(VI) reduction. These results are of significance because the reduction of soluble U(VI) to insoluble U(IV) is an important mechanism for the immobilization of uranium in aquatic sediments and the formation of some uranium ores. Furthermore, stimulation of microbial U(VI) reduction could be a useful mechanism for the bioremediation of uranium-contaminated waters.

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[1] Water Resources Division, U. S. Geological Survey, Reston, Virginia.

EFFECT OF IMPURITIES IN GYPSUM ON CONTAMINANT TRANSPORT AT PINAL CREEK, ARIZONA

Pierre D. Glynn[1]

ABSTRACT

Secondary gypsum is present in alluvial sediments at the Pinal Creek acid mine drainage site near Globe, Arizona. The gypsum forms from reaction of the acidic ground-water plume with detrital carbonate minerals, and contains impurities that reflect the composition of the contaminated water. Distribution coefficients measured for strontium, sodium, and magnesium agree with previously published results for gypsum coprecipitation from brines. Measured impurity mole-fractions are very small (strontium, 0.051 percent; sodium, 0.044 percent; aluminum, 0.04 percent; iron, 0.026 percent; potassium, 0.0075 percent; vanadium, 0.00701 percent; magnesium, 0.004 percent; manganese, 0.002 percent; molybdenum, 0.002 percent; barium, 0.0014 percent; chromium, ≈ (approximately) 0.0009 percent; cobalt, ≈ 0.0008 percent; nickel, ≈ 0.002 percent; copper, less than 0.001 percent; cadmium, 0.00018 percent; lead, ≈ 0.00016 percent). Theoretical considerations suggest that these impurities do not significantly change the solubility product of gypsum. Nevertheless, the molybdenum, vanadium, barium, strontium and cadmium impurities are high enough, relative to the contaminated water concentrations, that they may have to be considered in modeling reactions and transport of these elements at the Pinal Creek site.

Results of analyses of strontium (Sr) in carbonate rocks from formations surrounding the Pinal Creek valley, together with results of analyses of Sr in gypsum precipitated in the aquifer, suggest that the Sr increase that accompanies the neutralization of acid-contaminated ground water does not come solely from the dissolution of carbonate minerals. Feldspar dissolution is suggested as a significant source of Sr to the acidic ground water. A budget of the redox-independent reactions capable of consuming or releasing protons to the water is constructed using the Sr mass balance.

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[1] U.S. Geological Survey, Reston, Va.

Solid-phase variations in an aquifer as the aqueous solution changes, Globe, Arizona

By Walter H. Ficklin[1], Alonza H. Love[1], and Clara S.E. Papp[1]

ABSTRACT

Copper, manganese, zinc, calcium, aluminum, and sulfate were extracted from solid-phase material in the Pinal Creek aquifer. Sequential extractions were used to reveal phase associations of the above constituents in the coatings of the aquifer material. Grab samples were collected from five split-spoon drill holes in the background and in contaminated areas of the aquifer. The aquifer is contaminated with heavy-metal-laden acid mine water from an adjacent copper mine. Manganese oxides are forming at the water table. Apparently, calcium sulfate is precipitating. On the basis of increasing copper concentrations with time, heavy metals are concentrating on the grains as acidity increases because of the depletion of the aquifer carbonates with the acid water.

1. U.S. Geological Survey, Denver, Colorado

Solute transport in perennial streamflow at Pinal Creek, Arizona

By James H. Eychaner[1]

ABSTRACT

Black manganese (Mn) oxide precipitates in a 5-kilometer-long perennial-flow reach of Pinal Creek. Samples collected March 6-8, 1990, from streamflow and shallow ground water at 11 sites showed that through the reach pH increased 1.5 units, Mn decreased 80 percent, and dissolved inorganic-carbon concentration decreased 45 percent. A conservative-mixing model using only ground-water analytical concentrations adequately represented most constituents in streamflow. A reaction-path model using the computer program, PHREEQE, specified carbon dioxide degassing, Mn precipitation, and calcite dissolution to represent pH, Mn, and inorganic-carbon trends. The model could be improved by considering details of carbon dioxide degassing, ion exchange, gypsum and silica reactions, diurnal variation in reaction rates, and biological activity.

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[1] U.S. Geological Survey, Tucson, Arizona.

MANGANESE MINERALS AND ASSOCIATED FINE PARTICULATES IN THE PINAL CREEK STREAMBED

by Carol Lind, U.S. Geological Survey, Menlo Park, CA

ABSTRACT

Recently formed black manganese crust from the Pinal Creek streambed was sized and the magnetic and nonmagnetic parts of each fraction were segregated. Hot hydrochloric acid extraction showed that the iron to manganese molar ratios were 5 to 10 in the 150- to 250-μm (micrometer) particles but were much less than 0.1 in the nonmagnetic fractions of the 150- to 250-μm particle surface-layers, the 0.1- to 10-μm particles washed off the 150- to 250-μm particles, and the sieved 0.1- to 10-μm particles. Chemical analysis and X-ray diffraction (XRD) information suggest a mixture of $(Ca,Mn^{2+})Mn^{4+}{}_4O_9$-hydrate and $(Mn^{2+},Ca)Mn^{4+}{}_4O_9$-hydrate. The identity of the carbonate is questionable. Of the patterns for the carbonate mineral(s) that might be present, the XRD pattern for calcian kutnahorite $(Ca_{0.74}(Mn,Mg)_{0.26}CO_3)$ matched the sample pattern best. XRD patterns of particles from which manganese solids were removed indicated the presence of plagioclase, quartz, and lesser amounts of mica and chlorite. The manganese oxides obscured the plagioclase and the chlorite in the less than 75-μm fractions.

MEASUREMENT OF STREAM REAERATION AT PINAL CREEK, ARIZONA

By Steve A. Longsworth[1]

ABSTRACT

A measurement of stream reaeration at Pinal Creek, Arizona, was used to determine the carbon dioxide desorption rate. In the perennial reach of Pinal Creek, degassing of carbon dioxide and ingassing of oxygen appear to control precipitation of manganese oxides, which affects the movement and mobility of other metal compounds. After preliminary field work in January and March 1990, rhodamine WT dye and propane tracers were injected and sampled in a 2.1-kilometer reach in December 1990. Stream velocities in December were 73 to 181 percent greater than the velocities measured in March, even though discharge was 7 to 24 percent less. Less than 25 percent of the injected dye was recovered. The measured propane desorption coefficient was 1.63 per hour at 15.0 °Celsius for the 1.0-kilometer reach between sampling points. At 20.0 °Celsius the rate coefficients were 1.84 per hour for propane, 2.55 per hour for oxygen, and 2.28 per hour for carbon dioxide. The values are uncertain because of the limited available reach length and travel time, and the small amount of dye recovered.

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[1] U.S. Geological Survey, Tucson, Arizona

APPLICATION OF MINTEQA2 TO THE SPECIATION OF CONTAMINANTS AT GLOBE, ARIZONA

Kevin J. Novo-Gradac[1] and Charles N. Smith[2]

ABSTRACT

The geochemical speciation model MINTEQA2 was applied to study the movement of highly acidic contaminants through a carbonate-bearing aquifer underlying a mine waste site at Globe, Arizona. The MINTEQA2 code (Allison and others, 1990) was modified to allow the aquifer to be represented as a column through which a finite amount of contaminated water was allowed to pass. The distribution of contaminants among dissolved, adsorbed, and precipitated phases was tracked as a function of distance and the volume of acidic water that passed through the column. This type of modeling allows for an estimation of total contaminant loading within the column and forecasting of breakthrough events. This approach and its computer code may have further applications in the evaluation of *in-situ* remediation options.

[1] AScI Corporation, Athens, GA.

[2] Environmental Research Laboratory, U.S. EPA, Athens, GA.

SIMULATION OF COPPER, COBALT, AND NICKEL SORPTION IN AN ALLUVIAL AQUIFER NEAR GLOBE, ARIZONA

By Kenneth G. Stollenwerk[1]

ABSTRACT

Acidic water with elevated concentrations of metals has contaminated an alluvial aquifer near Globe, Arizona. Reactions between alluvium and acidic ground water were first evaluated in laboratory column experiments. The geochemical equilibrium speciation model MINTEQA2 was then used to simulate the observed changes in concentration of aqueous constituents in the column breakthrough curves. Attenuation of copper, cobalt, and nickel in the column experiments was a function of pH and could be quantitatively modeled by the diffuse-layer surface-complexation model in MINTEQA2. Intrinsic equilibrium constants for sorption of copper and nickel on ferrihydrite were obtained from the sorption literature: for copper, $\mathrm{LogK}^{int} = 0.6$; for nickel, $\mathrm{LogK}^{int} = -2.5$. The intrinsic equilibrium constant for cobalt was fit to the column experimental data; $\mathrm{LogK}^{int} = -2.0$.

The geochemical model was then used to simulate the observed changes in concentration of aqueous constituents along a flow path in the aquifer. Attenuation of copper, cobalt, and nickel along the flow path was simulated reasonably well using the diffuse layer model and the same intrinsic equilibrium constants used to simulate the column data.

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[1] U.S. Geological Survey, Denver, CO

STABILITY AND TRANSPORT OF INORGANIC COLLOIDS THROUGH CONTAMINATED AQUIFER MATERIAL

Robert W. Puls[1], Robert M. Powell[2], and Terry F. Rees[3]

ABSTRACT

Laboratory columns using contaminated natural aquifer material from Globe, Arizona, were used to investigate the transport of inorganic colloids under saturated flow conditions. Fe_2O_3 radio-labeled spherical colloids of various diameters were synthesized and introduced into the columns under varying conditions of pH, ionic strength, electrolyte composition, and colloid concentration. Column influent and effluent were evaluated by photon correlation spectroscopy and scintillation-counting techniques. Effluent breakthrough concentrations of the colloid were as high as 57 percent of the influent concentration under certain conditions. In all cases where significant transport occurred, the colloids arrived at approximately the same time as a conservative tracer, tritium. Conditions favoring colloidal transport in this system were low ionic strength and a pH in the range where the colloids are stable. Arsenate was used as a model reactive contaminant to evaluate its facilitated transport on the Fe_2O_3 colloids. The calculated sorption capacity of the colloids from batch tests was 1 percent by weight for arsenate. Compared to dissolved arsenate transport in the same columns, the colloids were transported more than 21 times faster.

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[3] USGS, San Diego, CA

Ground-water transport of polycyclic aromatic hydrocarbons in association with humic substances in the Pinal Creek basin, Globe, Arizona

By Robert W. Wallin[1], R.L. Bassett[1], and James H. Eychaner[2]

ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) are present in ground water in the Pinal Creek basin near Globe, Arizona. The maximum concentration of quantified PAH in samples from monitoring wells was 35 micrograms per liter. PAH contamination was found in a plume about 11 kilometers long. The source probably is in an area of active mining operations several kilometers upstream from the sampled wells. Concentrations of quantified PAH in the aquifer decrease significantly as the pH rises above 4.1. Concentrations of dissolved organic carbon (DOC) decrease in the same area. The fractions of the DOC that decrease are predominantly dissolved humic substances (DHS). Analyses of the data indicate that partitioning of PAH onto DHS could be taking place and the removal of PAH could be controlled by the adsorption of DHS onto metal hydroxides.

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[1] University of Arizona, Tucson, Arizona.

[2] U.S. Geological Survey, Tucson, Arizona.

HYDROCHEMICAL ZONING IN THE PINAL CREEK ALLUVIUM

by Gary R. Walter[1] and James R. Norris[1]

ABSTRACT

Acidic water is present in the alluvial aquifer along Pinal Creek near Globe, Arizona, as a result of mining and mineral processing in the Globe Mining District. Vertical and lateral variations in lithology and water chemistry were defined at four cross sections in the Pinal Creek alluvial valley on the basis of samples collected from boreholes. Analyses of these samples show that the most acidic water is confined to the lower part of the alluvium. Large differences in pH may result from density stratification and neutralization reactions. Neutralized water is present throughout the alluvium, and differences in dissolved solids concentration result primarily from dilution by recharge waters.

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[1] Hydro Geo Chem, Inc., Tucson, Arizona.

AQUIFER RESTORATION UNDER THE CLEAN WATER ACT

By Greg V. Arthur[1] and Shirin Tolle[1]

ABSTRACT

The Clean Water Act can be used to cause a responsible party to restore an aquifer if there is proof of a connection between the contaminated ground water and impacted surface waters. The Clean Water Act's advantages are its speed and ease of application.

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Mapping Subsurface Organic Compounds Noninvasively by their Reactions with Clays

by
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ABSTRACT

One of the most difficult tasks at hazardous waste sites is the mapping of organic contamination. The geophysical technique, complex resistivity, has been shown (Olhoeft, 1986) to be useful for mapping some organics through their reactions with clay minerals, although the processes being observed are commonly unknown. Laboratory evidence (King and Olhoeft, 1989) indicates that toluene in contact with montmorillonite is physically adsorbed onto the surface of the clay, coordinating with the exchangeable cations on the clay surface, becoming a cationic radical, and polymerizing in the vicinity of the Lewis Acid surface of the clay. This clay-catalyzed polymerization is consistent with known data from polymer chemistry and the electrochemistry of the cationic polymerization of toluene. These laboratory results explain the field data from the Willow Springs hazardous waste site, Calcasieu Parrish, Louisiana, (Olhoeft, 1986; Trudeau et al., 1988), and demonstrate that complex resistivity measurements can map the presence of toluene (where it is in contact with clay) noninvasively through the electrochemical signature of the montmorillonite-toluene polymerization.

An Automated Method to Quantify Physical Basin Characteristics

James J. Majure[1] and David A. Eash[1]

ABSTRACT

A method has been developed to automate the process of quantifying physical basin characteristics. This method will be used to quantify physical basin characteristics for correlation with surface-water quality within drainage basins. The method employs a combination of two software packages. The first package processes digital elevation data for the land surface and generates three geographic information system (GIS) data sets for a basin representing (1) the drainage network, (2) elevation contours, and (3) the surface-water drainage divide. The second package is a set of programs that quantifies 27 basin characteristics from the three previously generated GIS data sets.

In order to evaluate the accuracy and efficiency of the automated method, comparison data sets are being generated by two additional measurement methods at three different map scales. Preliminary comparisons with basin characteristics generated from manual measurements indicate that, with a few exceptions, the automated method can produce reliable results. Limitations inherent to the scale of the digital elevation data appear to account for most of the differences in the quantifications generated using the automated method. The automated method provides a significant reduction in the time required to quantify physical basin characteristics.

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[1] U.S. Geological Survey, Water Resources Division, Iowa City, IA, 319-337-4191

The Effect of Surfactants and Emulsions on Water Solubility of Organic Contaminants

D.E. Kile and C.T. Chiou
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Apparent water solubilities of 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT), 2,4,5,2',5'-pentachlorobiphenyl (PCB), and 1,2,3-trichlorobenzene (TCB) were determined at room temperature in aqueous solution of linear alkylbenzenesulfonate (LAS) surfactant and some commercial petroleum sulfonates. Petroleum sulfonates form stable emulsions in water that behave like a bulk organic phase in solubilizing organic solutes. The extent of solubility enhancement is linearly proportional to the concentration of the petroleum sulfonate-oil emulsion (PSO), in contrast to a sharp inflection in the vicinity of the critical micelle concentration (CMC) for a conventional (micelle forming) surfactant. The partition constant of the solute between the PSO and water is significantly higher than that between ordinary surfactant monomers below CMC and water. When the value is normalized for the nonpolar content of the emulsion, it approximates the solute's octanol - water partition coefficient (K_{ow}). Similarly, the much greater solubility enhancement of solute by LAS below the CMC than by monomers of conventional surfactants is attributed to a surfactant - oil emulsion formed as a result of the 1.7% neutral oil content in commercially formulated LAS. These neutral oils are comprised of linear alkylbenzenes (LABs) and di(alkylphenyl)sulfones. The oil-surfactant emulsion formed constitutes approximately 9 to 10 weight percent of the total LAS below CMC. Enhancement data for LAS above the CMC is comparable to those for other surfactant micelles. The data suggest the potential impact of surfactant-emulsion systems at low concentrations on the transport of organic contaminants in the environment.

Analysis of Atrazine Metabolites by Enzyme-linked Immunosorbent Assay and Gas Chromatography/Mass Spectrometry

by

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ABSTRACT

Enzyme-linked immunosorbent assay (ELISA) and gas chromatography/mass spectrometry (GC/MS) methods were developed and tested for the principal metabolites of atrazine, which include hydroxyatrazine, deisopropylatrazine, deethylatrazine, and didealkylatrazine. Methods developed included determination of cross reactivity by ELISA, an isolation by solid-phase extraction, and analysis by either ELISA or GC/MS. The cross reactivity of the metabolites by ELISA was slight compared to that of the parent compound atrazine; 50-percent inhibition values were 0.4 µg/L (micrograms per liter) for atrazine, 28 µg/L for hydroxyatrazine, and 30 µg/L for deisopropylatrazine and deethylatrazine. No cross reactivity was found for didealkylatrazine. The loss of alkyl side chains resulted in decreased cross reactivity. The metabolites were isolated from water on a carbon-18 (C_{18}) solid-phase cartridge for GC/MS analysis. Adsorption capacity factors for the metabolites decreased with increasing water solubility; didealkylatrazine had the least capacity. GC/MS was attempted on each of the metabolites; however, both didealkylatrazine and hydroxyatrazine required derivatization with pentafluropropionic anhydride before GC/MS analysis.

COMPARISON OF MICROTITRE-PLATE, ENZYME-LINKED IMMUNOSORBENT ASSAY (ELISA) AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) FOR ANALYSIS OF HERBICIDES IN STORM-RUNOFF SAMPLES

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ABSTRACT

Enzyme-linked immunosorbent assay (ELISA) for triazine and chloro-acetanilide herbicides was used as an inexpensive screening tool for storm-runoff at nine stream sites in the Midwestern United States. Microtitre-plate ELISA was chosen to provide semiquanitative analysis of herbicide concentrations in storm-runoff and to select sample subsets for analysis by gas chromatography/mass spectrometry (GC/MS). In comparing microtitre-plate ELISA concentrations to GC/MS concentrations, ELISA was found to be an effective measure of triazine herbicides in storm-runoff samples. However for chloro-acetanilides (alachlor and metolachlor), ELISA showed a number of false positives and cross reactivity with a metabolite that was not detected by GC/MS. The correlation coefficients between the triazine ELISA and GC/MS results were about 0.9 for atrazine and 0.8 for sum of triazines for the range of 0 to 3 µg/L (micrograms per liter). Thus, the microtitre-plate ELISA provides a good relative measure of storm-runoff concentrations of triazine herbicides for that concentration range. Samples with concentrations greater than 3 µg/L require dilution. Additional work is needed to evaluate the effectiveness of the ELISA as a semiquanitative measure of chloro-acetanilide herbicide concentrations in storm-runoff samples.

DESCRIPTION OF WATER-QUALITY SYNOPTIC EXPERIMENTS IN THE COLORADO RIVER

BY HOWARD E. TAYLOR[1] AND ROBERT C. AVERETT[1]

Synoptic experiments provide a way of assessing the water quality of complex large river systems. An example is presented of the use of the synoptic approach for assessing water quality along 290 miles of the Colorado River (Lake Powell through the Grand Canyon to Columbine Falls). The results of the synoptic study will be used to design future research studies and experiments on the various hydrologic processes impacting the Colorado River ecosystem.

[1] U.S. Geological Survey, Arvada, Colorado

EFFECTS OF GEOCHEMICAL FACTORS ON REMOBILIZATION AND REDEPOSITION OF CONTAMINATED BED SEDIMENTS IN BAYOU D'INDE, LOUISIANA

by Kurt L. Johnson and Jerry A. Leenheer[1]

ABSTRACT

Contaminated bed sediment from Bayou d'Inde, a tributary of the lower Calcasieu River, was elutriated with water of different salinities to determine the effects of geochemical factors on remobilization and redeposition of sediment. As the salinity decreased from 3.0 to 0.2 ppt (parts per thousand), the amount of suspended sediment forming stable colloidal suspensions increased from 0.06 to 8.27 percent. Colloid mineralogy was predominately quartz at 3.0 ppt salinity. At 0.2 ppt salinity the mineralogy changed to predominately smectite, with lesser quantities of kaolinite, illite, and quartz. At 0.2 ppt salinity, concentrations of halogenated organic compounds in resuspended sediments generally were lower than the concentrations in the remaining bed sediment.

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[1] U.S. Geological Survey, Baton Rouge, Louisiana

Overview of Research on Contamination of the Subsurface by Crude Oil at the Bemidji, Minnesota, Toxic Substances Research Site.

by

Marc F. Hult

ABSTRACT

The U.S. Geological Survey Toxic Waste Hydrology Program began an interdisciplinary research project in 1983 at the site of a crude oil spill near Bemidji, Minnesota. This paper provides a general description of the site and describes project objectives, history and organization. The spill occurred in 1979 when a pipeline transporting crude oil broke. After cleanup efforts were completed in 1980, about 400,000 liters of oil remained in the unsaturated zone and near the water table. This continues to be a source of contaminants to a shallow outwash aquifer. The oil is migrating as a separate fluid phase, as dissolved petroleum constituents moving with ground water, and as vapors in the unsaturated zone. Native microbes are converting the petroleum derivatives into carbon dioxide, methane, and other biodegradation products. The objective of the project is to improve understanding of the mobilization, transport, and fate of crude oil in the shallow subsurface. Research is conducted within four broad disciplines by researchers from the U.S. Geological Survey's National Research Program, Districts of the U.S. Geological Survey Water's Resources Division and Geologic Division, and several academic institutions. Currently, 20 research projects are active.

U. S. Geological Survey, St. Paul, Minnesota

Air, Oil, and Water Distributions at a Crude-Oil Spill Site, Bemidji, Minnesota

H.I. Essaid[1], W.N. Herkelrath[1], and K.M. Hess[2]

ABSTRACT

As part of a research program aimed at improving our understanding of immiscible-fluid movement in the subsurface, we developed a methodology for determining oil, water, and air saturation distributions in the subsurface. The method was tested at a crude-oil-spill site near Bemidji, Minnesota. Relatively undisturbed sediment cores were collected with a 1.5-meter-long piston core barrel at seven locations along a 120-meter longitudinal transect through the more southerly of the two oil pools. In order to immobilize the fluid phases, the core was rapidly frozen to below -60 degrees Celsius, in an alcohol bath cooled with dry ice, then immediately cut into approximately 7.8-centimeter lengths. The core sections were capped and sealed for laboratory analysis of fluid contents. Oil, water, and air contents of the samples were determined gravimetrically. The oil was extracted using strips of porous polyethylene that absorb oil but not water. The samples were then oven-dried to remove the water. After fluid-saturation analysis, particle-size distributions were determined for each sample.

On the basis of the field data, a clearly defined oil lens floats on the water table. The center of the oil lens has depressed the water table, and the flanks of the lens have migrated within the capillary fringe. There is poor correspondence between thicknesses of oil in wells and the actual distribution of oil in the subsurface. Sediment heterogeneity appears to play an important role in the distribution of the oil phase. The data were used to test a cross-sectional, multiphase flow model. Results of simulations indicate that the observed oil lens cannot be reproduced considering only the uniform mean properties of the sediments. Representations of observed spatial variability were incorporated into the model, illustrating the sensitivity of oil saturation to heterogeneity of sediment properties. The simulated oil lenses reproduce the general features of the observed lens, but do not reproduce the details of the subsurface oil distribution.

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1. U.S. Geological Survey, Menlo Park, CA
2. U.S. Geological Survey, Marlborough, MA

Field Validation of Conceptual Models of Mobilization and Transport of Volatile Petroleum Derivatives in the Unsaturated Zone near Bemidji, Minnesota

by

Marc F. Hult [1], Matthew K. Landon [2],
and Hans Olaf Pfannkuch [2]

ABSTRACT

A conceptual model of the mobilization, transport, and fate of volatile petroleum hydrocarbons in the unsaturated zone at the site of a crude oil spill near Bemidji, Minnesota, is presented. The model is based on field data from long-term, interdisciplinary research that began at the site in 1983. The major features of the contaminant plume in the unsaturated zone can be explained by assigning each major chemical constituent to one of three groups based on their sources, transport paths, and fate: (1) C3-C8 alkanes, (2) benzene and alky-benzenes, and (3) methane. C3-C8 alkanes are the least complex group. They comprise about 85 percent of the contaminant mass, their source can be characterized by a single partitioning term, and their movement is not strongly coupled with ground-water flow because water-soil gas interchange is not a major factor. Benzene and alky-benzenes are of intermediate complexity. Their high aqueous solubility causes them to partition to and be transported with ground water. Consequently, oil/gas, oil/water, and gas/water partitioning and concentrations in ground water must be known. The most complex group consists of methane which is produced in the unsaturated and saturated zones under anaerobic conditions. Therefore, two biologic rates need to be specified, which, in turn, depend upon substrate concentrations controlled by saturated- and unsaturated-zone processes.

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GEOCHEMICAL MODELING OF ORGANIC DEGRADATION REACTIONS IN AN AQUIFER CONTAMINATED WITH CRUDE OIL

Mary Jo Baedecker[1] and Isabelle Cozzarelli[1]

ABSTRACT

Crude oil from a pipeline break accumulated as an oil body at the water table in an aquifer near Bemidji, Minnesota. Hydrocarbons from crude oil were transported downgradient and a contaminant plume formed. The chemical composition of the ground water in the contaminant plume is significantly changed by the aerobic and anaerobic degradation of hydrocarbons and dissolution and precipitation of minerals. The mass transfer for chemical reactions that occurs at a point beneath the oil body to 40 meters downgradient from the oil body was calculated. The results of the mass-transfer calculations indicate that the major processes are the degradation of hydrocarbons, loss of carbon dioxide and methane to the unsaturated zone and into the atmosphere, dissolution of calcite and iron and manganese oxides, and precipitation of silica and an iron-rich carbonate.

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MECHANISMS CONTROLLING THE TRANSPORT OF ORGANIC CHEMICALS IN SUBSURFACE ENVIRONMENTS

George R. Aiken[1], Paul D. Capel[2], Edward T. Furlong[1],
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ABSTRACT

Ground-water contamination by anthropogenic organic chemicals is a significant problem in many areas. In areas of chemical spills, hydrophobic organic compounds have been shown to migrate farther than would be expected on the basis of chemical properties and traditional mass-transport theory. This has been observed for phenanthrene at a site contaminated with crude-oil near Bemidji, Minnesota. A conceptual multi-phase model is proposed, which includes equilibrium transport of the chemicals in the vapor phase and in the aqueous phase. Aqueous transport can occur either in the thermodynamically dissolved phase and in association with mobile "particles" (colloids, dissolved organic carbon (DOC), DOC-iron complexes, and oil droplets). Stationary particles (the geologic matrix) in the saturated and unsaturated zones attenuate transport by sorption. This conceptual model is used as a framework to discuss past and future investigations of transport of hydrophobic organic chemicals at the study site near Bemidji, Minnesota.

OVERVIEW OF SAN FRANCISCO BAY ESTUARY TOXIC CONTAMINANTS STUDY

By Kathryn M. Kuivila, U.S. Geological Survey,
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ABSTRACT

The San Francisco Bay estuary receives diverse synthetic organic and inorganic contaminants that vary widely in their environmental behavior, sources, seasonality, and toxicity. The objectives of this study are to (1) determine how organic contaminants from riverine and local sources are transported and transformed under varying hydrologic conditions (2) determine the ultimate fate of these organic contaminants and (3) develop approaches to determine whether contaminants influence ecological processes within this river-estuary system.

The primary determinants of organic contaminant distribution in the river-estuary systems are the geographic location of the source(s), the biogeochemical properties of the contaminants, and the hydrology of the system. Field studies will measure the distribution of several types of contaminants in the water column, sediments, and biota. These results, combined with laboratory studies of the biogeochemical properties of specific contaminants (for example, pesticides) and hydrodynamic modeling, can then be used to estimate distributions of organic contaminants under different conditions or in other environments.

TRANSPORT AND TRANSFORMATION OF DISSOLVED RICE PESTICIDES IN THE SACRAMENTO RIVER DELTA, CALIFORNIA

By Joseph L. Domagalski and Kathryn M. Kuivila,
U.S. Geological Survey, Sacramento, California

ABSTRACT

A large quantity of pesticides and herbicides are applied to flooded rice fields in the Sacramento Valley, California, during April, May, and June. Residues of molinate, thiobencarb, carbofuran, and methyl parathion have been detected in the Sacramento River and are of concern because of their effect on aquatic life. A Lagrangian study of the transport and transformation of these compounds was made along a 45-mile reach of the Sacramento River and the tidally influenced delta. Slow degradation rates of molinate, thiobencarb, and carbofuran resulted in conservative transport during the 4-day time frame of the study. In contrast, methyl parathion apparently was degraded in the rice fields to para-nitro phenol and only this product was detected.

ASSESSING ADVERSE EFFECTS OF CONTAMINANTS AT THE SAN FRANCISCO BAY TOXICS SITE by Samuel N. Luoma, James Carter and Cynthia L. Brown, U. S. Geological Survey, Mail Stop 465, 345 Middlefield Road, Menlo Park, CA

Examples of adverse effects from metal exposure can be found in aquatic benthic environments at all levels of biological organization (biochemical, physiological, population, community). Conclusively demonstrating such effects in moderately contaminated environments in nature can be challenging, however. The significance of responses to metals observed at low levels of organization is difficult to demonstrate. Conclusively proving that responses at higher levels of organization are attributable solely to metal exposure is also an important challenge. Studies that do not adequately characterize pollutant exposures and do not adequately consider either the influences of environmental history or the influences of stressors other than metals can yield ambiguous results. Understanding how metals affect aquatic benthos might ultimately require studying biological responses across several levels of organization and progressively building understanding of the affected environment over time. A multidiscipline study is using this approach in assessing effects of organic and inorganic contaminants on benthic species in San Francisco Bay.

OVERVIEW OF RESEARCH ACTIVITIES ON THE MOVEMENT AND FATE OF CHLORINATED SOLVENTS IN GROUND WATER AT PICATINNY ARSENAL, NEW JERSEY

by Thomas E. Imbrigiotta[1] and Mary Martin[1]

ABSTRACT

The U.S. Geological Survey is conducting an interdisciplinary research study of ground-water contamination by chlorinated solvents and other contaminants at Picatinny Arsenal, New Jersey. This paper summarizes the results of hydrogeologic and ground-water-contamination studies and describes ongoing research activities at the Building 24 site at Picatinny Arsenal.

Laboratory soil-microcosm studies were used to investigate the rates of reductive dechlorination of trichloroethylene and cis-1,2-dichloroethylene at the site. After an adaptation period of 18 weeks, most sites exhibited some degradation of cis-1,2-dichloroethylene; the maximum rate of transformation was observed at a location slightly beyond the midpoint in the flow system.

Results of laboratory column experiments showed that trichloroethylene transport in the unsaturated zone during infiltration is a nonequilibrium process. A field comparison indicated that the highest recovery of trichloroethylene from unsaturated-zone water was achieved by either collecting the sample in a gas-tight syringe or by purging and trapping the sample onsite.

A quasi-three-dimensional, finite-difference ground-water flow model of the glacial sediments and bedrock in the southern one-third of the Arsenal was used to estimate hydraulic conductivity and to describe the ground-water-flow system at the contaminant site. The two-dimensional solute-transport model, SUTRA, was modified to simulate the transport of energy and an unlimited number of chemical species subject to user-defined chemical reactions or biological interactions.

Twenty-four wells installed in 1989 in the area of Building 24 increased the well network to 74 wells which were sampled to define in detail the contaminant plume. Results of sampling showed that neither the areal and vertical extent of the plume nor the trichloroethylene concentrations have changed significantly since October 1987.

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CHEMICAL EVIDENCE OF PROCESSES AFFECTING THE FATE AND TRANSPORT OF CHLORINATED SOLVENTS IN GROUND WATER AT PICATINNY ARSENAL, NEW JERSEY

by Thomas E. Imbrigiotta[1], Theodore A. Ehlke[1], and Mary Martin[1]

ABSTRACT

Results of chemical analyses of ground water, soil gas, and aquifer sediments from a contaminant plume near Building 24 at Picatinny Arsenal, New Jersey, suggest that the fate and transport of chlorinated solvents, particularly trichloroethylene, are controlled by physical, chemical, and biological processes at the site. Nonaqueous-phase flow of trichloroethylene is suggested by both high concentrations of this contaminant near the base of the aquifer and preliminary results of solute-transport modeling. Relatively constant trichloroethylene concentrations near the source from 1987 to 1990 indicate the occurrence of slow desorption of trichloroethylene from contaminated aquifer sediments and (or) dissolution of nonaqueous-phase trichloroethylene in the aquifer. Detection of cis-1,2-dichloroethylene and vinyl chloride in 75 percent of the wells in the plume is indicative of biologically mediated reductive dehalogenation of trichloroethylene. Evidence of methanogenesis was found in 85 percent of the wells in which anaerobic reductive dehalogenation took place.

[1] U.S. Geological Survey, 810 Bear Tavern Road, Suite 206, West Trenton, New Jersey

BIOTRANSFORMATION OF CIS-1,2-DICHLOROETHYLENE IN AQUIFER MATERIAL FROM PICATINNY ARSENAL, NEW JERSEY

By Theodore A. Ehlke[1], Thomas E. Imbrigiotta[1],
Barbara H. Wilson[2], and John T. Wilson[3]

ABSTRACT

Soil cores were collected within and adjacent to a trichloroethylene plume that has contaminated the shallow aquifer at Picatinny Arsenal, New Jersey, to study the rate of cis-1,2-dichloroethylene biotransformation. Soil cores also were collected at a highly contaminated site within the plume to determine the effect of different electron donors on the rate of cis-1,2-dichloroethylene biotransformation under methanogenic conditions. Ground-water samples were analyzed for volatile organic compounds to study the relation between volatile-organic-compound concentrations and the biotransformation of cis-1,2-dichloroethylene. Biotransformation in microcosms from sites within the plume ranged from slight to more than 90 percent after an incubation period of 32 weeks. The most extensive biotransformation in soil microcosms occurred at a site near the highest in situ cis-1,2-dichloroethylene concentration measured at the Arsenal (710 micrograms per liter). Biotransformation was negligible at an uncontaminated site. Amendment of soil microcosms with combinations of methanol, formate, toluene, p-cresol, propionate, and butyrate inhibited the biotransformation of cis-1,2-dichloroethylene. A combination of methanol and formate had the greatest inhibitory effect.

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[2] Rice University, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma

[3] U.S. Environmental Protetion Agency, Ada, Oklahoma

SIMULATION OF REACTIVE MULTISPECIES TRANSPORT IN TWO-DIMENSIONAL GROUND-WATER-FLOW SYSTEMS

by Mary Martin[1]

ABSTRACT

A model code, developed by modifying an existing two-dimensional nonreacting solute-transport model to simulate the transport of an unlimited number of species subject to user-defined chemical reactions and sorptive processes, is described. Simulation results that duplicate previously published results, and simulations of simultaneous solute and energy transport and of hydrocarbon transport and degradation, show that the code accurately simulates multispecies movement and interaction and is a useful tool for the analysis of contaminant fate and transport.

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[1] U.S. Geological Survey, West Trenton, NJ

The chemistry of silica-organic complexation in a petroleum-contaminated aquifer

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ABSTRACT

Organic substances generated by microbial activity in a petroleum contaminated sand and gravel aquifer accelerate the rate of silicate dissolution and increase the solubility of quartz. Experimental investigations of quartz dissolution experiments show that some simple organic acid-anions accelerate quartz dissolution at circum-neutral pH below 70 degrees celsius. Silica-organic complexes were found in aqueous solution using Ultraviolet, Raman and Infrared spectroscopic methods, with both a hydrogen bonded and siloxane bonded complex identified. Molecular orbital modeling of potential complex-structures suggest that both types of bonding are possible, and that a critical factor is the O-Si-O bond angle. Modeling of solution complexes offers insight into the mechanism of dissolution rate enhancement by suggesting possible surface-activated complexes.

EVOLUTION OF PHYSICAL PROPERTIES AND COMPOSITION OF CRUDE OIL AT A SPILL SITE

By Matthew K. Landon[1] and Marc F. Hult[2]

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ABSTRACT

The spatial distribution and characteristics of crude oil spilled August 20, 1979 have been monitored since 1983 at the Bemidji, Minnesota Research Site. Oil has migrated at least 30 meters as a separate fluid phase in a glacial-outwash aquifer and is losing soluble and volatile compounds through dissolution into ground water and vaporization into the unsaturated zone. Spatial differences in the physical properties and composition of the oil have developed owing to alteration of the originally uniform source. Gas chromatographic headspace analysis shows that the oil is selectively losing compounds with low molecular weights, mainly alkanes, through volatilization. Oil samples subjected to volatilization under controlled conditions in the laboratory show systematic relationships between viscosity, specific gravity, vapor pressure, refractive index, and composition similar to those exhibited by field samples. Observed changes in physical properties of crude oil at the site reflect yearly oil-mass loss rates from 0 to 1.25 percent (average 0.5 percent) and total losses from the original oil mass as high as 11 percent (average 3.8 percent). Temporal and spatial variations in the physical properties and composition of crude oil at the Bemidji site from 1984-1989 are not uniform and suggest that alteration rates are highly variable. The refractive index of oil can be used as a surrogate measure of mass loss and composition using samples as small as a single drop, thereby permitting mass loss to be calculated for oil droplets from cores. This work provides a method of quantifying rates of loss from the crude oil source, a critical step in calibrating transport models of volatile and soluble constituents.

KINETICS OF CRUDE-OIL BIODEGRADATION BY BACTERIA INDIGENOUS TO SEDIMENT AND GROUNDWATER

Fu-Hsian Chang[1], Hai Wang[2], Brenda Denzin[1] and Julie Bullert[1]

ABSTRACT

In this study, static and microcosm systems were used to conduct biodegradation experiments of crude-oil by indigenous microorganisms over a period of 6 months. Kinetic models were developed to predict rates of biodegradation of crude-oil in ground-water environments. The Monod equation was applied to describe the rate of substrate consumption by indigenous crude-oil-degrading bacteria grown in static or microcosm system.

Four assumptions were made in this study: (1) crude-oil is solubilized before its assimilation; (2) final products help the dissolution and mineralization of crude-oil; (3) biodegradation occurs by metabolism and cometabolism simultaneously; and (4) numerous populations of indigenous microorganisms are capable of utilizing crude-oil and other carbon sources present in the sediment/ground water.

A variety of environmental factors were examined to determine their effect on biodegradation kinetics of crude-oil: the concentration of crude-oil, redox potential (or dissolved oxygen), availability of inorganic nutrient (such as nitrogen and phosphorus), population density of crude-oil degrading bacteria and temperature of the environment. In order to simplify the kinetic study the temperature parameter was treated as an independent variable and the other five parameters were treated as interdependent. Five differential equations were proposed to describe their interrelationships. They were solved by the fourth-order Runge-Kutta numerical method. The maximum specific growth rate (U_{max}) and turnover time (T_{ov}) were 0.092 to 0.291 per hour and 1.57 to 4.35 days, respectively, in samples treated with 200 mg/L of crude-oil; and 0.051 to 0.207 per hour and 1.72 to 4.49 days, respectively, in samples treated with 400 mg/L crude-oil. Yield coefficients (Y) increased with increasing temperature, they were 0.12 to 0.41 and 0.14 to 0.47 for samples treated with 200 mg/L and 400 mg/L crude-oil, respectively. Both U_{max} and rate constant for the disappearance of the substrate (K_s, in μg/L) increased with rising incubation temperature and decreased with increasing substrate concentrations. The maximum biodegradation rate (V_{max}) ranged from 5.93 to 17.39 (μg/mL)/h, whereas the rate constant (K_t) varied from 0.51 to 0.99 μg/mL. Both V_{max} and K_t increased with increasing incubation temperature.

This study indicated that the biodegradation rate conformed to fourth-order kinetics which may be as appropriate as second-order kinetics for biodegradation studies when values for environmental factors are not known, and maybe more appropriate than second-order kinetics when values for environmental factors are known.

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Factors Controlling Mass Transfer at an Organic-Liquid/Ground water Interface

by

H.O. Pfannkuch[1], L. F. Guo[1], and M.F. Hult[2]

ABSTRACT

Conceptual analytical and physical models of hydrocarbon dissolution are presented. A physical plate model representing a typical petroleum spill was constructed using a porous medium of a well-sorted quartz sand, with a hydraulic conductivity of about 10^{-4} m/s, and average water velocities ranging from 10^{-6} to 10^{-3} m/s. Mass-transfer characteristics for benzene, toluene, m-xylene, and binary mixtures were determined. Conceptual and analytical models show that there is a critical aquifer thickness below which mass transfer from a floating hydrocarbon source is restricted. The primary mass transfer mechanism is dissolution driven by a concentration gradient. For thin aquifers, the plume of dissolved constituents may reach the bottom of the aquifer, thereby reducing the concentration gradients and, therefore, dissolution rates. Results of the physical modeling demonstrate the velocity and solubility dependence of the mass-transfer coefficient consistent with the analytical solutions. The plate model results show that the proportion of benzene dissolving from a benzene-toluene mixture decreased by a factor of 2 after 20 pore volumes. These experiments demonstrate that the composition of the petroleum source will change through time, and, therefore, the concentrations entering ground water will also change. Extension of the conceptual model to three dimensions suggests that differential dissolution would be the most pronounced at the periphery of the hydrocarbon body and that dissolution would also depend on the geometry and orientation of the hydrocarbon body with respect to the flow field.

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[2] U.S. Geological Survey, St. Paul, Minnesota

Quantitative Statistical Description of Subsurface Heterogeneities with Ground Penetrating Radar at Bemidji, Minnesota

by
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ABSTRACT

Ground penetrating radar cross sections of the Bemidji, Minnesota, research site show details of the subsurface stratigraphy with resolution on the order of 20 centimeters to depths of 20 meters. Computer processing of the radar images has been applied to correct for the geometric distortions of the data acquisition process. Statistical analysis of the lengths of horizontally connected structures in the radar cross sections show significant geological heterogeneity across the site. In particular, the axis of one of the two petroleum plumes beneath the site (the main plume) coincides with a statistical boundary between horizontal structure lengths that are 40 meters or shorter and those that are 80 meters and longer. Parts of the site also exhibit anisotropy in the distribution of horizontal structure lengths.

SOURCES IN CRUDE OIL OF NONVOLATILE ORGANIC ACIDS DOWNGRADIENT FROM AN OIL BODY AT BEMIDJI, MINNESOTA

K.A. Thorn[1] and G.R. Aiken[1]

ABSTRACT

Nonvolatile organic acids have been isolated from contaminated wells downgradient from an oil body and from an uncontaminated well upgradient from the oil body, at Bemidji, Minnesota. The nonvolatile organic acids from contaminated and uncontaminated wells were characterized by elemental analyses, molecular-weight determinations, ^{14}C dating, and ^{13}C and ^{1}H nuclear magnetic resonance (NMR) spectrometry. The undegraded oil, and the saturate, aromatic, resin, and asphaltene fractions of the undegraded whole crude oil, also were analyzed by ^{13}C and ^{1}H NMR spectrometry. The nonvolatile organic acids isolated from the contaminated wells were clearly distinguishable from those isolated from the uncontaminated well. The nonvolatile organic acids downgradient from the oil body appear to be derived from the C_{18} or greater aromatic, branched chain, and cyclic components of the crude oil.

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[1] U.S. Geological Survey, Denver, Co.

REDUCTIVE DECHLORINATION OF TRICHLOROETHYLENE IN ANOXIC AQUIFER MATERIAL FROM PICATINNY ARSENAL, NEW JERSEY

by

Barbara H. Wilson[1], Theodore A. Ehlke[2],
Thomas E. Imbrigiotta[2], John T. Wilson[3]

ABSTRACT

Ground water at Picatinny Arsenal, New Jersey, has been contaminated with chlorinated solvents released from the wastewater-treatment system and the degreasing-unit relief system of a metal-plating facility. Trichloroethylene is the major contaminant but 1,1,1-trichloroethane and tetrachloroethylene are also present. Cis-1,2-dichloroethylene and vinyl chloride were not original contaminants, but their accumulation in the ground water indicates reductive dechlorination of the trichloroethylene and tetrachloroethylene released to the aquifer. Laboratory microcosms were used to estimate the kinetics of reductive dechlorination at field scale. The microcosms were constructed with aquifer material collected from locations along the longitudinal axis of the plume and from outside the area of contamination. To determine whether supplementary electron donors would enhance reductive dechlorination, three suites of electron donors were added to microcosms: (1) butyrate, propionate, toluene, and p-cresol; (2) butyrate, propionate, formate, methanol, toluene, and p-cresol; and (3) formate and methanol.

Preliminary results indicate that both sorption and biological processes are important removal mechanisms. First-order rate constants in the microcosm study ranged from 0.004 to 0.02 per week and compared favorably to estimated first-order rate constants of 0.03 to 0.09 per week calculated from field data. Reductive dechlorination was not enhanced in microcosm experiments in which alternate electron donors were added.

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[2] U.S. Geological Survey, West Trenton, New Jersey.
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Comparison of four methods for sampling and analyzing unsaturated-zone water for trichloroethene at Picatinny Arsenal, New Jersey

James A. Smith[1], H. Jean Cho[2], Peter R. Jaffé[2],
Cecilia L. MacLeod[1], and Susan A. Koehnlein[1]

Four methods of collecting samples of unsaturated-zone water for quantitative analysis for trichloroethene (TCE) were compared at Picatinny Arsenal in Morris County, New Jersey. For all four methods, water is transferred from a depth of 2 meters to land surface with a 0.15-meter-long suction lysimeter attached to a 1.85-meter length of 0.32-centimeter-outer-diameter stainless-steel tubing. For the first method (standard), water flows from the lysimeter into a 5-milliliter glass serum vial with a Teflon-lined septum cap. Sample is withdrawn from the vial through a second line leading to a water trap and vacuum source. After 15 to 20 milliliters of water passes through the serum vial, the vial is disconnected and returned to the laboratory for analysis. For the second method (modified Bengt-Arne Torstensson), a vacuum line is connected to a 5-milliliter serum vial with a Teflon-lined septum cap. After causing a negative pressure of approximately 95 centibars, the vacuum is disconnected from the vial and the vial is connected directly to the stainless-steel tubing leading to the lysimeter. The negative pressure in the vial induces flow from the lysimeter to the vial. The water sample in the vial is transported to the laboratory for analysis after flow stops. For the third method (syringe), water flow is induced by vacuum from the lysimeter through a port connector attached to silicone tubing. The needle of a 5-milliliter gas-tight syringe is inserted through the silicone tubing so that the tip of the needle extends into the port connector. As water passes the tip of the syringe needle, the plunger of the syringe is extended to draw a sample into the barrel of the syringe. After sample collection, a Mininert valve at the end of the syringe is closed and the sample is transported to the laboratory in the syringe for analysis. For the final method (purge-and-trap), water flow is induced into a purge vessel by vacuum. An adsorbent trap is placed between the effluent end of the purge vessel and the vacuum source to capture TCE that volatilizes from the water sample. TCE remaining in the water sample is purged onto the trap with helium and the trap is transported to the laboratory for analysis. All samples are analyzed for TCE by gas chromatography. Statistical analysis of the data indicates that either the purge and trap or syringe methods can more accurately collect water samples from the vadose zone for quantitative analysis for TCE relative to the modified Bengt-Arne Torstensson or standard methods.

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SIMULATION OF GROUND-WATER FLOW AT PICATINNY ARSENAL, NEW JERSEY

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ABSTRACT

Ground-water flow in the glacial sediments and bedrock at Picatinny Arsenal was simulated with a quasi-three-dimensional, finite-difference ground-water-flow model. Geophysical logs, lithologic logs, particle-size data, and test cuttings from selected wells were analyzed to identify six permeable layers and five intervening, low-permeability layers for simulation purposes.

Results of ground-water-flow simulation indicate that flow directions change in response to seasonal fluctuations in recharge rates. When ground-water-recharge rates are high, simulated flow in the water-table aquifer in the area of building 24 at the arsenal is toward Green Pond Brook, and ground water flows toward the arsenal at the southern boundary. When recharge rates are low, simulated flow in the water-table aquifer in the area of building 24 is toward Green Pond Brook, but has a slight downvalley component; simulated ground-water flow in the water-table aquifer at the arsenal's southern boundary is away from the arsenal and downvalley to Rockaway Creek. These simulated ground-water-flow directions suggest the possibility of advective movement of contaminants in these areas.

Results of particle tracking analysis indicate that the distribution of trichloroethylene in the building 24 area is not exclusively controlled by flow paths in the upper part of the unconfined aquifer, even when apparent dispersion caused by seasonal variations in the flow paths is considered. The difference between flow paths in the permeable layers in the upper and lower parts of the unconfined aquifer also affects the distrubution of contaminants in the building 24 area.

Based on calculated ground-water velocities near the building 24 area, a conservative solute would be flushed from the ground-water system in approximately 250 to 550 days; however, contaminant concentrations in observation wells located in a contaminant plume near building 24 have remained constant since the source was removed in 1985. Therefore, processes other than advective movement are involved with the transport of contaminants at this site.

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DESIGN OF A FIELD EXPERIMENT TO STUDY THE DYNAMICS OF TRICHLOROETHYLENE VAPORS IN THE UNSATURATED ZONE DURING AN INFILTRATION EVENT

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ABSTRACT

Laboratory experiments are being conducted to examine the transport of volatile organic compounds in the unsaturated zone during infiltration. Measurements of the concentration profile of trichloroethylene (TCE) in soil air and soil water, and of the moisture profile within the soil are being taken. Preliminary data have shown that nonequilibrium phenomena are important in mass transport in two-phase (gas, water) laboratory soil systems during infiltration. A field experiment at Picatinny Arsenal in Morris County, New Jersey, is being planned to examine these processes on a field scale. When scaling an experiment from the laboratory the field, natural spatial variability can be significant. Therefore, an examination of the variability in soil-water TCE concentrations in the field has been conducted. It has been found that spatial and temporal variability in soil-water concentrations are significant at Picatinny Arsenal, and that spatial variability is pronounced when sampling probes are located one meter from one another.

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CHARACTERIZATION OF HIGH MOLECULAR WEIGHT COLORED COMPOUNDS IN GROUND WATER AT PICATINNY ARSENAL, NEW JERSEY

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ABSTRACT

A zone of dark-colored ground water containing a high dissolved organic carbon content has been found in water from a well directly adjacent to a pipe that discharged chlorinated solvents directly into the unsaturated zone of the aquifer beneath Picatinny Arsenal, New Jersey. The zone of colored water has moved from the point of discharge to a second well about 90 feet downgradient. Fulvic acids have been isolated from samples of the colored waters from both wells and from water from a background well that has not been affected by the discharge of chlorinated solvents. The nuclear magnetic resonance spectra of the fulvic acids from the colored waters are very similar, but are markedly different from the nuclear magnetic resonance spectrum of the fulvic acid from the background well. It has been tentatively concluded that the colored waters are soil pore waters that have been displaced by dense chlorinated solvents discharged into the unsaturated zone.

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