ENVIRONMENTAL FORUM 1990:

Geoscience Investigations That Emphasize Chemical, Physical, and Biological Ecosystem Processes

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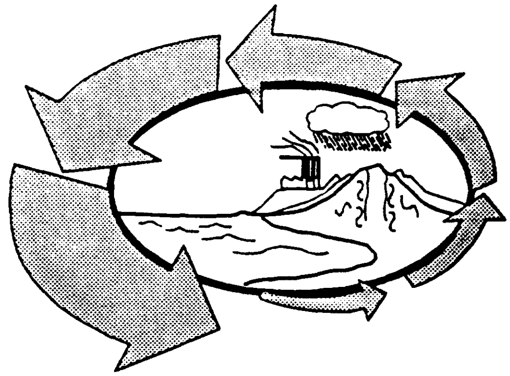

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Additions to the Open-File Report (not included on the program):

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Introduction

L.P. Gough

Although the U.S. Geological Survey is known for research on mineral resources, its research on the consequences of mineral extraction and use deserve equal attention. Many of the geochemical and geophysical studies that investigate near-surface geological processes have direct application to the research of current environmental problems that are of national interest. These processes involve our mineral, soil, water, air, and vegetation resources.

One of the Survey's greatest assets is its long tradition of excellence in research and in reporting scientific information; as an agency we have sometimes failed, however, to adequately communicate both our long history of contributions to the solution of environmental problems and our ability to help solve urgent environmental challenges. This forum, therefore, has two main objectives: (1) to inform individuals, organizations, and agencies of the types of environmental geoscience studies being conducted by the Geologic Division, and (2) to elicit feedback from participants on any new research directions the Division should consider.

The studies in this report were chosen to represent a general cross section of research being conducted within the Geologic Division of the USGS. This one-day activity is meant to initiate a process that will result in a series of forums with more specialized agendas.

Although geologic hazards research has enjoyed emphasis in the past and remains important, new areas of environmental geoscience studies include rock/water, soil/water, and even plant/soil investigations. Specific areas of environmental research reported here include: acid-mine drainage, wetlands, metal mobility in surficial environments and uptake by vegetation, remote sensing, ecosystem dynamics, trace-element kinetics, point and non-point sources of contamination, geochemical and geophysical analytical methods development, and laboratory standards research. Many of these studies have great problem-solving "cross-over" potential, and the processes and techniques discussed can be used to tackle broad-scale problems such as global/climate change and subsurface contamination.Many of the authors may allude to the "quick-fix" mentality that exists in our society toward remedial activities aimed at "solving" a particular environmental problem. This approach should be a concern to everyone because decisions and policies that are made without a firm foundation in research are costly at best and may even be unhealthy. Daniel E. Koshland, Jr. (Science, vol. 247, p. 777, 1990) stated "Part of a more rational approach to confronting environmental problems is to rely more on facts and be willing to modify policies as new facts are uncovered." The USGS is an agency that specializes in providing facts.

Processes Controlling Trace-metal Cycling in the Environment

L.S. Balistrieri and T.T. Chao

Physical, biological, and chemical processes are responsible for the distribution and mobility of elements in the environment. These processes include mixing and diffusion, biological uptake and release, sorption by particulate matter, precipitation, anthropogenic inputs, fluxes across phase or chemical boundaries, and redox cycling. The complexity of natural systems usually requires determining the relative importance of several processes for a given metal. This requires adequate geochemical tools. A good geochemical tool set should include biological, chemical, and physical methods for determining such entities as bulk composition, element speciation, solid phase associations, mineral assemblages, as well as thermodynamic and kinetic models. The use of these tools can provide an understanding of the important processes and thereby the information necessary to predict the response of elements to changing biochemical conditions and to formulate plans for preventative and/or remedial action.

This talk will focus on the response of elements to changing redox conditions. In so doing, all of the above processes except the input of anthropogenic elements will be addressed. Trace-metal data from a seasonally anoxic system will be used to demonstrate the various responses of elements to changing redox potential and to illustrate the processes responsible for metal cycling in the environment.

Applications of Light Stable Isotopes to Environmental Problems

G.S. Plumlee

Stable isotope studies of light elements have broad applications to environmental problems. Stable isotopes are of greatest use for understanding the operation of natural geochemical cycles (especially those of oxygen, hydrogen, sulfur, carbon, and nitrogen) and for tracing how those cycles have been affected by man. The U.S. Geological Survey (USGS) has laboratory facilities for studying a variety of stable isotopes, and scientists with extensive research experience in the application of stable isotopes to environmental and other geochemical problems. This paper presents a brief review of environmental stable isotope studies by USGS and other researchers. For a detailed review, the reader is referred to the multi-volume *Handbook of Environmental Isotope Geochemistry* (1980-1988, Fritz and Fonts, eds., Elsevier), or general texts on the subject.

Background. Isotopes of a naturally-occurring element have the same number of protons in the nucleus but different numbers of neutrons. Different elements have various combinations of stable isotopes (such as Oxygen-16 (^{16}O) and ^{18}O) and/or radiogenic isotopes (such as uranium-238 (^{238}U), ^{235}U, and ^{234}U, which undergo radioactive decay). Individual isotopes of an element are distributed differentially between chemically reacting compounds or coexisting phases due to their subtle differences in mass; the smaller the atomic weight of the element, the greater the isotopic fractionation. The isotopic composition of a compound is generally measured by comparing the ratio of the heavy (less abundant) isotope to the lighter (more abundant) isotope in the compound to the same ratio in a standard. Isotopic compositions are given as parts per thousand or per mil (‰) variations. For example, the isotopic composition of sulfur is given as:

$$\delta^{34}S‰ = 1000 \text{ x } [((^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{standard}) - 1].$$

Although the radiogenic isotopes have extensive applications in environmental studies, this paper will focus on the stable isotopes of light elements commonly found in the environment, including hydrogen, oxygen, carbon, sulfur, and nitrogen.

Hydrogen and oxygen. Stable isotopes of hydrogen (^{1}H, deuterium [^{2}H or D]) and oxygen (^{16}O, ^{18}O) fractionate extensively during evaporation and precipitation of water. Evaporation produces isotopically light water vapor, which is fractionated to even lighter isotopic compositions by subsequent precipitation; this fractionation increases at greater distances inland from the oceans, at higher latitudes, at higher elevations, or in colder climates or seasons (average ocean water is 0‰ δD and $\delta^{18}O$; surface waters in coastal Calif. are near -30‰ δD and -5‰ $\delta^{18}O$; surface waters in the central Rocky mountains are near -130‰ δD and -17.5‰ $\delta^{18}O$; snow in Antarctica can be as light as -428‰ δD and -56‰ $\delta^{18}O$). Groundwater can retain the characteristic isotopic composition of its source surface water or can undergo isotopic shifts in response to processes such as reactions with aquifer rocks or mixing with isotopically distinct waters from a different aquifer.

Hydrogen and oxygen isotopes have been used extensively in hydrology applications. The isotopic composition of ground water is very useful for identifying source areas where an aquifer is recharged: ground water derived from local precipitation would have a different isotopic signature than that derived from a distant source at higher elevations. "Old" ground waters recharged under different climatic conditions are isotopically distinct from those recharged more recently. Seasonal isotopic variations in an aquifer suggest rapid recharge rates from nearby sources. The extent of aquifer recharge by surface waters can be elucidated by measurement of isotopic variations in ground water away from rivers or lakes. Relative discharges of tributary rivers can be estimated indirectly from isotopic measurements of water in the tributaries and water downstream from the confluence.

The hydrogen and oxygen isotopic compositions of minerals and vegetation are also very useful for determining past variations in climate conditions, such as temperature and precipitation, because they record changes in the isotopic composition of ground and surface waters over time. For example, the hydrogen isotopic composition of tree rings and the oxygen isotopic composition of carbonate minerals in ancient soil horizons have both been used extensively in paleoclimatic and global-warming studies.

Sulfur. Sulfur in the environment originates from a wide variety of sources via a complex array of inorganic, biological, and anthropogenic processes. Many of these sources and processes are marked by characteristic sulfur isotope (^{32}S and ^{34}S) signatures that allow the discrimination of sulfur originating from different sources and/or processes. Most sulfide sulfur of deep-seated origin (i.e., that in igneous rocks, igneous-related ore deposits, volcanic gases, etc.) is near 0‰. In contrast, present-day oceanic sulfate is isotopically heavy (near 20‰ $\delta^{34}S$), as are marine evaporites (> +10‰ $\delta^{34}S$) formed in the past. Bacterially mediated reduction of marine sulfate can lead to extreme sulfur isotope fractionations; these fractionations are reflected in the isotopically variable composition of sulfides in sedimentary rocks (from < -40‰ to > +40‰), sulfides in coal (-30‰ to +30‰), and sulfur in petroleum (-10 to +20‰).

Sulfur isotopes are helpful for sorting out the various sources and sinks for sulfur in individual ecosystems. These include entrained sea spray, organic sulfur compounds (released from microorganisms and plants), sulfur from volcanic emissions, anthropogenic pollutant sulfur, sulfate in rainfall, and sulfate in continental dust.

Sulfate formed through kinetically-controlled oxidation of sulfide generally inherits the isotopic signature of the parental sulfide, and is thus very useful for tracing the source of aqueous sulfate in the environment. For example, sulfur isotope studies can be used to discriminate sulfate formed through oxidative weathering of igneous sulfides (near 0‰), sulfate formed from oxidation of volcanic gases (near 0‰), sulfate derived from marine evaporites (> +10‰), and sulfate formed through oxidation of sedimentary sulfides (isotopically light or heavy).

The sulfur isotopic composition of coals, oils, or sulfide ores is generally maintained during combustion or roasting. The isotopic compositions of atmospheric sulfur dioxide and resultant sulfate in acid rain have been used successfully to fingerprint specific oil/coal-fired power plants or smelters that produced the sulfur dioxide.

The oxygen isotopic composition of sulfate provides further constraints on the sources of the sulfate and the mechanisms by which it formed. For example, sulfate formed in the presence of abundant atmospheric oxygen (i.e., on a weathering mine dump or in a mine with rapid flowthrough of oxygenated surface water) has isotopically heavy oxygen, whereas sulfate formed in the subsurface (i.e., in a mine filled with standing water) has isotopically light oxygen derived from the ground waters.

Carbon. Carbon isotopes (^{12}C, ^{13}C) can be used to differentiate potential sources for carbon and the chemical processes which affect carbon in the environment. Marine carbonate is defined to be 0‰ $\delta^{13}C$. Reduced carbon (such as methane or carbon in organic matter) is strongly enriched in the light isotope (-10 to -80‰ $\delta^{13}C$), methane derived by bacterially mediated reduction is generally lighter than -50‰, and atmospheric CO_2 is moderately enriched in the light isotope (-7‰ $\delta^{13}C$). CO_2 in magmas formed by melting of average mantle materials is near -5‰ $\delta^{13}C$. Processes leading to isotopic fractionation of carbon include inorganic redox processes and a variety of biological processes.

The isotopic composition of aqueous carbonate can give clues as to whether it originated by oxidation of organic matter (from -10 to -50‰), by bacterial action (methane with -50 to -80‰), by input from the atmosphere (near -7‰), by addition of volcanic CO_2 (near -5‰, or by dissolution of marine carbonate rocks (near 0‰). Carbon isotopes can be used to evaluate the extent of degradation of organic contaminants in ground waters via bacterial action or reaction with aquifer rocks. Carbon isotopes have also been used to establish the relative proportions of methane in the atmosphere from various sources (including termite emissions, decaying organic matter, etc.). Carbon isotopic studies of volcanic lakes in Africa by USGS scientists have shown that extremely high CO_2 concentrations in the lake waters are due to input of CO_2 from deep magmatic sources rather than organic sources; catastrophic degassing of the lake waters has led to significant loss of human and animal life in the areas surrounding the lakes.

Nitrogen. The concentrations and isotopic compositions of nitrogen (^{14}N, ^{15}N) in the environment are largely controlled by biological activity and by nitrogen fixation through lightning discharges. Atmospheric N_2 is defined to be 0‰, and terrestrial plants have isotopic compositions between -10 to +10‰. In general, atmospheric ammonia, reduced and oxidized soil gases, soil organic matter, animals, and petroleum are enriched in the heavy isotope (up to +20‰ $\delta^{15}N$). Nitrogen in natural gas, sedimentary nitrate, and atmospheric nitrate are generally enriched in the light isotope (typically from 0 to -20‰ $\delta^{15}N$); however, natural gas can show positive enrichments as well.

Nitrogen isotope fractionations have been used with varying degrees of success to identify nitrate and ammonia from natural sources versus fertilizer sources in ground and surface waters. Nitrogen isotopes have also been used to distinguish sources of nitrogen in ocean systems from nitrogen in sewage. Because nitrogen plays an important role in nutrient cycling in the oceans, nitrogen isotopes are important tools in studies of climate change. Further research into environmental applications of nitrogen isotopes are likely to be highly productive.

Selenium--An Example of a Trace Element Greatly Affected by Human Activities

J.R. Herring

The bioessential elements participate actively in a multitude of natural inorganic and biochemical processes on Earth, and this participation is now altered by human activities. Current interest in the geochemical cycle of selenium has occurred because of the element's critical nutritional requirement in animals. It is, however, a mixed blessing due to both toxic effects, if assimilated in excess, and equally severe consequences when nutritionally deficient.

The natural, overall selenium geochemical cycle involves mainly crustal rock sources and oceanic sediment sinks. The crustal cycle is strongly influenced by biochemical reactions that mobilize or fix selenium in organic compounds. Four principal inorganic species exist: selenide (-2), elemental selenium, selenite (+4), and selenate (+6). Partitioning among these species in a particular environment depends largely on the pH and Eh conditions and to lesser extent on the availability of other ligand- and complex-forming species. Common oxidizing crustal conditions favor the presence of selenite and selenate. Selenate is the most soluble and also commands the most societal attention and concern because of its mobility and toxicity, as well as its ease of uptake in plants and animals. In contrast, anoxic or dysaerobic conditions favor the occurrence of selenide. The reduced species also occurs in organoselenium compounds, although the original metabolic uptake could include oxidized or reduced species.

Selenium behaves like sulfur more than like any other element; however, there is an important difference: selenium is more readily reduced than sulfur, or, conversely, sulfur is more readily oxidized than selenium. This allows divergence of their geochemical behaviors, particularly under strongly oxidizing conditions. For example, the ocean waters concentrate sulfate relative to selenate; oxidized, gaseous sulfur can form at high temperatures and disperse more readily than oxidized selenium.

Humans considerably modify this natural geochemical cycle by adding sources of selenium to the environment; these are principally coal combustion, sulfide ore processing, and waste processing from the industrial use of selenium. The recent discovery that certain irrigation practices in the western U.S. mobilize naturally occurring selenium and concentrate it in anoxic sediments has had a profound influence on the planning and construction of new water diversion projects. These man-induced selenium releases rival the natural releases and exemplify major human involvement in an element's geochemical cycle. The effect of the human perturbation on the selenium geochemical cycle, is to force natural, steady-state pathways and reservoirs towards new equilibria.

Adsorption of Toxic Substances onto Clays as Detected by Mid-infrared and Complex Resistivity Measurements

T.V.V. King and G.R. Olhoeft

One of the most difficult tasks at a hazardous waste site is the mapping of organic contamination. The geophysical technique, complex resistivity, sometimes maps organics through their reactions with clay minerals. Infrared spectroscopic evidence indicates that toluene (methylbenzene) in contact with montmorillonite is physically adsorbed onto the surface of the clay and coordinates with the exchangeable cations on the clay surface. In this process, the coordinated toluene loses a proton to become a cation radical. Mid-infrared and complex resistivity measurements suggest that the toluene radicals polymerize in the vicinity of the Lewis acid surface of the clay. The spectral data indicate that the polymerization is complete within 1 hour after preparing the toluene-clay mixture. The electrochemical evidence indicates that this adsorption and radical formation occurs rapidly (milliseconds or less). In this process the polymerization proceeds as oxidative coupling of toluene and is suspected to react to form methylphenyl-phenylmethane (Soma and others, 1985, J. Physical Chem., v. 89, p. 738-742), dibenzyl or polyphenylene. The polymerization process may be either diffusion or kinetic limited. Results of this laboratory study combined with the field data of Olhoeft (1986, Proc. NWA/API Conf. on Petrol. Hydrocarbons and Organic Chemicals in Ground Water, p. 284-305) demonstrate that complex resistivity measurements can noninvasively map the presence of toluene (where it is in contact with clay) via the electrochemical signature of the montmorillonite-toluene polymerization.

Geochemical and Biogeochemical Baselines and Backgrounds in Environmental Studies

R.C. Severson

Geochemical and biogeochemical *backgrounds* should represent natural concentrations, which ideally exclude man's influence. Geochemical and biogeochemical *baselines* represent a concentration specific to one place and time and are typically not true backgrounds. A background represents an idealized situation and is typically more difficult to measure than a baseline. True backgrounds may be obtained, for example, by sampling and analyzing tree rings, glacial ice cores, and varves from lake or ocean sediments.

Baselines and backgrounds are generally derived by the same procedures: (1) define the population to be described, (2) collect unbiased samples to represent the population, (3) analyze the samples for the constituents of interest, and (4) compute the values for background or baseline using statistical techniques.

Baselines and backgrounds are necessary in environmental studies to describe the geochemical or biogeochemical nature and variation of an environment, and to assess the extent, or intensity, of alteration to that environment by some external source. Examples of geochemical baselines, using different statistical techniques, will be given for the San Joaquin Valley, California; the Kendrick Reclamation Project Area, Wyoming; and the Kenai National Wildlife Refuge, Alaska.

In addition to environmental studies, baselines and backgrounds can also be used as a tool in mineral exploration, botanical studies, or geologic studies. In mineral exploration, the baseline or background can identify localities within an area that are geochemically or biogeochemically anomalous and thus of possible economic interest. In botanical or geologic studies, baselines or backgrounds provide information on the abundance and distribution of a constituent, which is necessary to understand local- or global-scale processes.

Examples and Modeling of Trace Metal Water/Sediment Partitioning in Colorado Streams Affected by Acid Mine Drainage

K.S. Smith, W.H. Ficklin, and J.F. Ranville

Basic understanding of mechanisms that govern trace metal partitioning and mobility in streams is essential to the determination and predictive modeling of environmental pathways. It has long been recognized that adsorption/desorption reactions control trace metal concentrations in many natural water/sediment systems. Adsorption of trace elements by hydrous iron oxides present in streams receiving acid-mine drainage may influence aqueous concentrations of these elements. Adsorption of cations and anions by oxide substrates is strongly pH-dependent. As pH increases, more cations and fewer anions are adsorbed onto oxide substrates. There is a narrow pH region, known as the adsorption edge, in which transition from essentially no adsorption to essentially complete adsorption takes place. This pH region is characteristic for the adsorbing ion as well as species concentrations and the solid substrates present. Adsorption reactions are included in several water equilibrium computer models. These models can be applied to the prediction of partitioning of trace metals in streams that receive acid-mine drainage.

Partitioning of trace metals between stream water and stream sediment has been examined both in St. Kevin Gulch, near Leadville, CO, and in Clear Creek downstream of Idaho Springs, CO. For water and bed sediment collected from St. Kevin Gulch, copper and zinc partitioning due to pH-dependent adsorption reactions have been accurately modeled using the MINTEQA2 computer model coupled with the MIT diffuse-layer adsorption model. For Clear Creek water samples collected in June, 1986, copper, manganese, and zinc exhibit pH-dependent partitioning between "dissolved" and suspended phases with a higher proportion of the "dissolved" phase at lower pH values.

Some Effects of Acid Mine Drainage on a Subalpine Wetland, Tennessee Park, Colorado

K. Walton-Day and B.M. Erickson

St. Kevin Gulch, a first-order stream impacted by acid-mine drainage, flows through a wetland before entering Tennessee Creek, a tributary to the Arkansas River. The wetland covers a 30 ha area and is primarily a sedge meadow. Two major ecosystems were identified: (1) sedges growing on top of hummocks (*Carex canescens L.*); and (2) sedges growing between or off hummocks (*Carex utriculata* Boott.). Using an unbalanced statistical sampling design, samples of peat and of both plant types were collected at 96 sites in the wetland. Chemical analyses showed the following mean concentrations of elements in peat samples (reported in ppm on a dry weight, whole-sample basis): aluminum, 47,000; calcium, 4,400; cadmium, 21; cobalt, 6; copper, 145; iron, 21,000; potassium, 11,000; magnesium, 3,200; manganese, 230; sodium, 2,400; nickel, 16; lead, 530; and zinc, 1,400. Mean concentrations of all elements are similar in both plant types and, except for potassium and manganese, are up to 3 orders of magnitude less than mean concentrations in peat samples. Mean concentrations of potassium and manganese are greater in plants than in the peat samples suggesting that the plants play a more important role than the substrate in removing manganese from the mine drainage. Plant and peat samples containing elevated concentrations of metals generally cluster: (1) where the stream channel loses its form and the water from St. Kevin Gulch spills onto the wetland; (2) where St. Kevin Gulch appears to have previously flowed onto the wetland through now-abandoned channels; and (3) at the lower end (mouth) of the wetland. In these areas, high metal concentrations are caused by metal loading from the acid-mine drainage. A zone of elevated metal concentrations in plant and peat samples located upstream of the St. Kevin Gulch input to the wetland may be caused by runoff from lands disturbed by previous mining activity or by upwelling ground water that has been in contact with mineralized rock.

The Geochemistry of Arsenic in the Cheyenne River System, South Dakota and the Clark Fork River, Montana

W.H. Ficklin

Arsenic sulfide minerals -arsenopyrite, orpiment, enargite and others- are oxidized to arsenite ((As(III)) and eventually to arsenate ((As(V)) on exposure to air and water. These arsenic entities are in turn adsorbed by iron oxyhydroxide, a common constituent of river sediment. When this sediment is deposited in a lake or reservoir, a series of bacterially mediated reactions dissolves iron oxyhydroxide releasing arsenate to interstitial water. Chemical conditions in the sediment column are such that arsenate is converted to arsenite which in turn may precipitate as an arsenic sulfide mineral.

Arsenic sulfide minerals are included with copper deposits at Butte, Montana and the Homestake gold mine at Lead, South Dakota. Because arsenic was not an economic mining product, it became part of the waste material. Enormous quantities of arsenic-bearing tailings were deposited in the headwaters of the Clark Fork River, Montana (400 million metric tons) and in Whitewood Creek, South Dakota (100 million metric tons). Whitewood Creek discharges into the Belle Fourche River which in turn discharges into the Cheyenne River, a tributary of the Missouri River. Dissolved arsenic concentrations of 40 ug/L were found in the water of the Clark Fork River in the summer of 1987. In Whitewood Creek the dissolved arsenic concentration varies from about 20 ug/L during high flow to about 120 ug/L during low flow. Samples of tailings collected near Butte, Montana contain up to 5000 mg/kg arsenic and tailings from overbank deposits on Whitewood Creek contain up to 4000 mg/kg arsenic. The sediment of each river contains arsenic also. Concentrations near 1000 mg/kg arsenic are found in samples of sediment from Milltown Reservoir. Arsenic concentrations in samples from Whitewood Creek are as great as 1100 mg/kg. In the Belle Fourche River arsenic concentrations in the sediment reach 250 mg/kg and in the Cheyenne River the concentration has diminished to about 30 mg/kg. Natural concentration of arsenic in uncontaminated streams ranges from about 5 to 10 mg/kg. Milltown Reservoir is a small lake formed by a hydroelectric dam at the confluence of the Blackfoot and the Clark Fork Rivers. The Cheyenne River enters Lake Oahe, near Pierre, S.D. and forms a narrow bay about 40 miles long. Thus each river has a sediment trap. Evidence for the cycle of arsenic from sulfide minerals to soluble arsenic entities and back to sulfide minerals is found in geochemical studies of the sediment of Milltown Reservoir and the Cheyenne River Embayment. Concentrations of As(III), as great as 8000 ug/L and 1600 ug/L, were found in the interstitial water of Milltown Reservoir and the Cheyenne River Embayment, respectively. Arsenic-III is the most toxic form of inorganic arsenic and it is an important intermediate product in the cycle of arsenic reactions. The geochemical conditions in the sediment columns of the reservoirs provide a pathway for ground water contamination with arsenic whenever the reservoir loses water through ground-water flow.

Rock/Water Interactions and Ground-water Contamination in Permian Rocks, Central Oklahoma Aquifer

G.N. Breit, E.L. Mosier, J.L. Schlottmann, and C.S.E. Papp

Future development of the Central Oklahoma aquifer, a major water source in central Oklahoma, may be limited because locally, water produced from the aquifer has large concentrations of certain toxic metals. The origin of these environmentally important concentrations is being investigated by a cooperative effort of the U.S. Geological Survey's Geologic and Water Resources Divisions as part of the National Water-Quality Assessment (NAWQA) Program. Goals of this multidisciplinary investigation are to understand processes that release arsenic, chromium, selenium, and uranium from the rocks into the ground water and to develop criteria for predicting the location of water with potentially hazardous concentrations. Our studies have focused on one aspect of this investigation--characterizing solid constituents of the aquifer.

The Central Oklahoma aquifer underlies approximately 3000 square miles and includes unconsolidated Quaternary alluvial deposits and Permian rocks composed of interbedded "red bed" sandstones, mudstones, and siltstones. Seven test wells were cored through the Permian rocks at different locations, one in an area of good water quality, and six in areas known to have large concentrations of arsenic, chromium, selenium, or uranium. Rock samples collected from the cores were analyzed by ICP-AES to determine the concentrations of 40 elements, selenium and arsenic abundances were determined by hydride generation, and uranium concentrations were measured by delayed neutron activation. The mineralogy of whole-rock samples and clay-sized separates was determined by X-ray diffraction. Detailed petrographic observations were made using standard optical techniques and scanning electron microscopy.

The rocks have average concentrations of 7.3 parts per million (ppm) arsenic, 56 ppm chromium, 1.4 ppm selenium (calculated for 346 of the 549 samples analyzed that have selenium contents greater than the 0.1 ppm detection limit) and 3.64 ppm uranium. Abundances as great as 62 ppm arsenic, 170 ppm chromium, 110 ppm selenium, and 123 ppm uranium were detected, although all metals are not enriched in any single sample. The enriched samples include isolated limonitic sandstone lenses and small "reduction spots".

Mineral constituents of the aquifer, listed in approximate order of abundance, are quartz, clay minerals, feldspars, hematite, dolomite, calcite, and goethite. Feldspars and carbonate cements have dissolution textures, which reflect interaction between these solids and the ground water. Extensive "flushing" of the aquifer in the area of generally good water quality is suggested by the relative absence of chlorite, plagioclase, and carbonate cements in these samples. This flushing may explain the small concentrations of arsenic, chromium, selenium, and uranium in water from this area.

The mobility of metals in both typical and enriched rocks was assessed using a $NaHCO_3$ partial extraction technique, a 5-step sequential partial dissolution procedure, and petrographic observations. The $NaHCO_3$ extraction technique was used to mimic waters in the aquifer and was effective in extracting small amounts of arsenic, selenium, and uranium. The sequential extraction procedure includes steps for dissolving metals contained in soluble (KCl), ligand exchangeable (KH_2PO_4), acid soluble (HCl), oxidizable, (HCl-$KClO_4$), and residual (HF-HNO_3-$HClO_4$) sites on or in solid phases. On average, 60 percent of the arsenic, 35 percent of the chromium, 75 percent of the selenium and 60 percent of the uranium contained in the rock were extractable (dissolved before the residual step). Appreciable amounts of arsenic, selenium, and uranium (> 10 percent) were dissolved in some samples by the soluble and ligand extractions. Therefore, a significant portion of these metals are in sites from which they are easily released. Petrographic observations are consistent with the extraction results and show that most extractable arsenic and chromium are associated with iron oxides, most extractable uranium may be bound to iron oxides and in uranium-vanadium minerals, and extractable selenium is present as selenium metal.

Our preliminary interpretations suggest that as recharge (mainly precipitation) moves through the aquifer its chemical composition changes. These changes are caused mainly by ion exchange with clay minerals and by dissolution of carbonate cements. Coupled with these changes, arsenic, chromium, selenium and uranium disseminated in the rock are oxidized by the water to more soluble forms. Efforts to better understand the processes responsible for the large concentrations of arsenic, chromium, selenium, and uranium in water from the Central Oklahoma aquifer are continuing.

Source of Trace Elements in Stream Sediments from the Upper Illinois River Basin, Illinois, Indiana, and Wisconsin

S.M. Smith and R.F. Sanzolone

The upper Illinois River basin is one of four areas of the United States selected to evaluate procedures and concepts for the surface-water phase of a National Water Quality Assessment (NAWQA) Program. The four major rivers in the basin are the Kankakee and the Des Plaines Rivers, which combine to form the Illinois River, and the Fox River. The 10,949-square-mile basin is dominated by agricultural land use (75%) and the Chicago metropolitan area (13%). Multivariate statistical techniques were applied in a synoptic study of stream sediments to describe the occurrence and distribution of major, minor, and trace elements in the basin.

The less-than-63-micrometer portion of stream sediments was analyzed for 47 constituents. Sediments were collected at 276 randomly selected sites on first and second-order streams to estimate natural occurrence and at 133 main-stem sites to characterize river-reach distributions and the effects of point sources on sediment content. R-mode factor analysis was applied to each data set for reduction into significant element associations or factors. A five-factor model for the first- and second-order stream data set and a four-factor model for the main-stem data set were chosen to help interpret the data.

Urban/industrial contamination, geology, and natural chemical sinks control the concentrations of heavy metals present in stream sediments within the basin. A strong anthropogenic influence was identified by a single factor, dominated by heavy metal elements, in each factor model. Anthropogenic sources and depositional environments were investigated by comparison of factors with a geologic base and single-element plots, and by additional factor analysis of anthropogenic elements identified in the four-factor model.

Geological Factors Affecting Radionuclide Mobility

R.B. Wanty, L.C.S. Gundersen, and R.R. Schumann

A research program funded by the U.S. Geological Survey, Department of Energy, and the Environmental Protection Agency is being conducted to investigate the geologic factors affecting radionuclide mobility in the natural environment. The primary focus of the program is Radon-222 (^{222}Rn) in soil gas and ground water, and the contribution of ^{222}Rn in each of these media to indoor airborne ^{222}Rn. When present in indoor air, ^{222}Rn is a suspected carcinogen. ^{222}Rn is a daughter in the uranium-238 (^{238}U) radioactive decay series; its immediate parent radionuclide is Radium-226 (^{226}Ra). Our results show that an integrated approach, including geologic, geochemical, and pedologic studies, is the most effective in understanding ^{222}Rn distribution in the environment. We hope to gain a reliable means of predicting areas likely to have problems with high levels of ^{222}Rn by examining the processes governing the mobility of ^{222}Rn as well as its radioactive parents.

Studies have been performed in a number of areas around the United States, including the Reading Prong, Pennsylvania, the Piedmont and Valley and Ridge of the Appalachian Mountains, the Atlantic and Gulf Coastal Plain, the northern Great Plains, and the Rocky Mountains. Our major conclusion is that there is a strong correlation between local geology and the potential for high ^{222}Rn in soil gas or ground water.

In the Piedmont and Reading Prong, shear zones (in particular mylonite zones) produce high ^{222}Rn concentrations because uranium is redistributed during ductile deformation from resistate minerals, which have a low degree of emanation, to more highly emanating sites in foliations and associated fractures. Uranium commonly is associated with iron and titanium oxide grain coatings. The high emanation of ^{222}Rn from the rocks to the soil gas or ground water causes the very high concentrations of ^{222}Rn found in soils, ground water, and homes associated with shear zones.

In areas underlain by sedimentary rocks, variable ^{222}Rn concentrations have been found in soil gas. For instance, in the Northern Great Plains, several types of continental glacial deposits were found to have high concentrations of ^{222}Rn in soil gas, resulting in a large proportion of homes with high indoor ^{222}Rn levels in Iowa, North Dakota, and Minnesota. In the Coastal

Plain of the eastern and southern U.S., generally low concentrations of ^{222}Rn are found in soil gas and homes. High soil-gas ^{222}Rn occurs in glauconitic sandstones, phosphatic claystones and sandstones, black shales, and heavy mineral sand deposits.

Soil and weather characteristics have a marked influence on radon generation and mobility in soils. Results of a study at the Denver Federal Center (DFC) showed that as much as a tenfold difference in soil radon concentrations may occur seasonally as a result of moisture capping effects and formation and destruction of desiccation cracks in the soil. Shorter term, two- to threefold variations in soil radon concentrations can occur in response to precipitation, barometric pressure, and other weather factors. Soil type is important in determining the magnitude of the soil's response to weather factors. Smectitic soils such as those found at the DFC site are most susceptible to the moisture capping effects noted in the study.

Investigations of ^{222}Rn in ground water supplies have shown that extremely high levels of dissolved ^{222}Rn occur in some areas. Equally important is the finding that high levels of uranium and radium also may exist in these areas. When present in high enough concentrations in drinking water, these elements pose a threat to human health. Adsorption processes appear to be the major control on the concentrations of uranium and radium, but radon concentrations seem to be limited by the degree of emanation of radon from the rock to the water as it is produced by radioactive decay of radium.

Future studies of radon in rocks and soils will concentrate on radon emanation and the climatic and geochemical parameters that most affect it. A nationwide study of granites and associated shear zones will attempt to further evaluate some of the most severe radon problems in the U.S. Studies of radionuclides in ground water will be directed toward a more thorough understanding of the geology, petrology, geochemistry, and hydrogeology of the rock-water system, and the chemical and physical factors influencing ^{222}Rn sources. In addition, a more reliable method for estimating the contribution of radon in domestic water to indoor air will be evaluated.

Electromagentic Methods for Environmental Monitoring and Sensing

D.L. Campbell, G.R. Olhoeft, D.C. Stewart, R.J. Bisdorf, B.D. Smith, and V.F. Labson

The Branch of Geophysics, USGS, has recently developed several electromagnetic (EM) techniques and instruments for use in groundwater and toxic waste studies. In order of increasing depth of penetration, these are: interpretative and display capabilities for ground penetrating radar; a high-frequency EM sounder; and airborne VLF and 60 Hz conductivity mapping tools. All EM techniques are sensitive to particular physical properties of the ground--electrical conductivity, dielectric permittivity, and magnetic susceptibility. The extent to which each of these properties plays a role depends on its magnitude and on the frequency of the EM system being used. Radar systems, typically having frequencies of 10 MHz and higher, are primarily sensitive to changes in dielectric permittivity, as at an interface between dry and wet soils. VLF and lower frequency systems (about 20 kHz and lower) are primarily sensitive to electrical conductivity. Because most surficial materials are not highly magnetic, the effect of magnetic susceptibility can usually be neglected; geologic units that are magnetic will typically masquerade as electrically conductive ones. An expert system program for MS-DOS computers has been written to choose between different geophysical methods that can be used to trace a plume of pollutant after a spill (Olhoeft, 1988, U.S. Geol. Survey Open-File Rept. 88-399, [MS-DOS floppy disk]).

Ground penetrating radar systems have been commercially available in this country for a decade, but their outputs have typically been limited to displays that could only be interpreted qualitatively. Computer programs have been written by the USGS to do high resolution displays and quantitative interpretations of such data. A multifrequency example from Sand Dunes National Monument, CO, shows detailed stratigraphy to depths of greater than 40 m with a resolution of 1 cm in the top 4 m decreasing to 10 cm at 40 m depth.

Airborne VLF (approximately 20 kHz), 60 Hz, and commercial EM systems can be used for areal mapping of ground conductivities at varying effective depths whcih depend on the operating frequencies. The USGS VLF and 60 Hz systems were recently flown over Palo Alto, CA, to map the saltwater-freshwater interface along the shore of San Francisco Bay. An example from

Brookhaven Oil Field, MS, shows a similar application where commercial airborne EM was used to help map brines that have contaminated shallow aquifers.

The high frequency sounder operates in the frequency range 300 kHz to 30 MHz. In this range both conductivity and dielectric permittivities effect the results, and for many geologic materials both vary in complex ways. Work is therefore proceeding on several fronts: measurements in the Petrophysics Laboratory to build a catalog of electric properties for different geologic materials; computer simulations of results to be expected when the materials are layered together in different ways; design and testing of electronic equipment to use in the field; and development of appropriate computer programs to interpret field data. An example from Palisades-Kepler State Park, IA, shows layering interpreted along a profile where the Water Resources Division, USGS, is testing for groundwater pollution by agricultural chemicals.

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USGS/DOI Irrigation Drainage Studies, Kendrick, Wyoming

J.G. Crock, J.A. Erdman, and R.C. Severson

Selenium in agricultural drainage is an environmental hazard at many irrigation projects in the western U.S. Our study seeks to (1) define the sources of selenium and its distribution in both agricultural and native plants and soils of the Kendrick Reclamation Project Area (KRPA) near Casper, Wyoming; and (2) evaluate the influence of irrigation on the selenium distribution in irrigated lands. Samples native soil and sagebrush (*Artemisia tridentata* Nutt.) were collected from 14 geological units in the study area. Samples of soil and alfalfa (*Medicago sativa* L.) were collected from 109 sections in the KRPA where >40 acres per section were under irrigation. Total and water-extractable selenium in soils and total selenium in plants were determined. Many samples of sagebrush and alfalfa had high selenium contents. About 15% of the alfalfa samples contained >4 ppm selenium--a level potentially hazardous to livestock if fed over extended periods of time. About 20% of the sagebrush samples contained >1.1 ppm selenium--the maximum reported selenium baseline in western U.S. sagebrush. In contrast, native and cultivated soils contained <0.1-3.3 ppm selenium, which is not unusual when compared with the baseline values established for soils of the Northern Great Plains. Landscape patterns for total selenium in alfalfa and water-extractable selenium in agricultural soils are displaced from total selenium in soils, due to ground water flow patterns.

USGS/NPS Air Quality Biomonitoring, Florida and California

L.L. Jackson and L.P. Gough

An interagency agreement has been in effect since 1983 between the U.S. Geological Survey (USGS) and the National Park Service (NPS) for the purpose of studying the influence of atmospheric anthropogenic trace metal and sulfur emissions on vegetation and soils in and near several national parks. Studies have focused on developing elemental baselines for assessing environmental degradation, examination of spatial trends of plant and soil chemistry with respect to point and non-point contamination sources, and biogeochemical processes that influence our ability to discriminate between elements of natural and anthropogenic origin.

In 1984, we studied plants and soils from Everglades and Biscayne National Parks and nearby areas in order to trace the influence of emissions from the Turkey Point power plant, the largest oil-fired electrical generating facility in the US at the time. We collected samples along traverses progressing away from the power plant and extending on to park lands. We were unable to satisfactorily discriminate between natural and anthropogenic sources or to define a zone of influence of the power plant based on the concentrations of about 20 trace elements and sulfur in vegetation. Due to the complexity of micro-ecosystems within a 30-km radius of the power plant, diverse natural processes occurring within each ecosystem obscured the influence of the power plant on element concentrations. Stable sulfur isotope ratios in plants and soils were more definitive in helping to elucidate the power plant influence. However, their interpretation was also confounded by the complexity of the sulfur cycles occurring in the various micro-ecosystems. We began additional studies in 1989 in Everglades National Park to study spatial trends in trace element chemistry in a slash pine community, a single, more homogeneous ecosystem.

Biogeochemical studies in the Santa Monica Mountains National Recreation Area near Los Angeles, California, were initiated in 1986. The recreation area is composed of 150,000 acres of public and private conservation lands that are easily accessible to more than 14 million people. The area is notorious for its photochemical smog, but is not heavily industrialized. The purpose of our study was to examine the spatial and temporal variations in trace element chemistry of two species of shrubs and soils in order to define the influence of non-point source emissions from the Los Angeles basin and surrounding metropolitan areas. A major aspect of this work was defining biogeochemical processes that influence our ability to discriminate between natural and anthropogenic sources to refine future research studies. In general, due to the complex physiographic and geologic nature of the Santa Monica Mountains, spatial trace-element trends are difficult to define. However, lead decreases in concentration by factors of 2-5 in both plants and soils westward away from the most populated areas along the 80-km range. Whereas it is reasonable to assume that the lead originates from automotive emissions, additional research is required to verify its source. Temporal trends in plant chemistry were dominated by the seasonal influence of nutrient cycling. The essential elements were most dramatically affected by seasonal cycling, but non-essential trace elements, such as lead, were impacted by this cycling as well. Plant chemistry may be affected seasonally by anthropogenic emissions due to climatic conditions; however, even non-essential elements appear to be influenced more by nutrient cycling in this ecosystem.

Data from these projects can be used to determine elemental baselines for comparison with future geochemical and biogeochemical changes. However, in ecosystems where anthropogenic emissions do not overwhelm natural processes, our ability to discriminate between natural and anthropogenic elemental sources is handicapped. Pilot projects with the NPS are important in helping to identify the elements and processes on which to focus additional research.

Selenium Sources in the Diablo Range, Western Fresno County, California

R.R. Tidball, R.C. Severson, T.S. Presser, and W.C. Swain

A selenium anomaly occurs in San Joaquin valley soils in western Fresno County, California. An investigation of the geologic source of this anomaly included reconnaissance sampling of soils and weathered rock material in several geologic formations in the vicinity of Monocline Ridge. The Ridge is a series of steeply dipping sedimentary beds ranging in age from Late Cretaceous to Quaternary that border the westside of the valley. In general, the nonmarine rocks of Pliocene and younger age tend to be nonseleniferous, and marine rocks of Oligocene to Upper Cretaceous age are variously seleniferous. The Tumey Formation of Oligocene age, the Kreyenhagen Shale of Eocene age, and the Moreno Shale of Late Cretaceous age contain the highest amounts of selenium. The wide range of selenium found, 2.5 to 12 ppm in the Tumey Formation, 0.8 to 35 ppm in the Moreno Shale, and 0.3 to 45 ppm in the Kreyenhagen Shale, indicates that the distribution is not uniform within these formations. Dissolved selenium appears to be concentrated where sulfate salts are precipitated either in seeps or in the sediments of ephemeral streams that receive drain water from these rocks. Dissolved selenium transported to the valley floor in muddy debris flows by ephemeral streams tends not to reach the ground water because of restricted through-flow potential. Dissolved selenium transported by intermittent streams, however, apparently recharges ground water and moves by artesian flow to the lower end of the alluvial fans.

The following abstracts were given at the *11th Annual Meeting of the Society for Wetland Scientists* in Breckenridge, Colorado on June 6, 1990. Although scheduling conflicts did not permit their inclusion in the Environmental Forum 1990, they are reproduced here because they complement the papers presented in the forum session entitled **Agency Case Studies.**

Origin of Sedimentation and Uranium in the Boston Peak Fen, North-central Colorado

J.K. Otton

The Boston Peak fen is located in the upper Laramie River valley 75 km west of Fort Collins, Colorado. The depression that hosts the wetland formed shortly after late Pleistocene glacial ice retreated from the valley floor. Unstable Tertiary sediments and moraine on the valley wall slumped onto the valley floor and dammed part of it. Water ponded in the 10-15 m deep depression and clay and silt accumulated. About 10,000 years ago, pond weeds became established, and organic productivity increased. About 3,000 years ago, downcutting of the spillway and infilling of the pond created conditions shallow enough for the establishment of peat-forming sedges. Up to 3.5 m of peat has accumulated. Recently, shrubs and willows have invaded the wetland. Initially, uranium derived from spring and shallow ground waters was adsorbed from the water by organic matter in the sediment to form layers ranging in uranium content from 10 to 150 ppm. As the wetland developed, ground water recharge zones (spring pools, marginal seeps) became point sources of metal input, and as much as 3,300 ppm uranium accumulated locally in the peat.

Hydrologic Setting of the Boston Peak Fen

R.R. Schumann

The Boston Peak fen is a montane lakefill wetland with ground water hydrology characterized by a confined, locally artesian aquifer overlain by an unconfined aquifer. Clayey glacial and postglacial lake sediments act as an aquiclude separating underlying glaciofluvial sands from overlying peat. Faults and fractures in the surrounding crystalline rocks act as conduits for uranium-rich waters that enter the wetland as seeps and springs, providing the primary water input to the wetland. Concentrations of uranium in the wetland are largely confined to areas along the margins and base of the wetland deposits, and along preferred ground water flow paths. Twenty piezometer stations consisting of 40 wells were used to measure hydraulic conductivity of wetland deposits, monitor water tables, and characterize ground water flow within the wetland. Seasonal water table fluctuations are unequal across the wetland and are reflected in the distribution of plant types: The area with the greatest seasonal water table fluctuation is a willow carr, whereas the area with consistently higher water tables is a sedge-dominated fen.

Geochemical Controls on the Distribution of Uranium in Sediments of the Boston Peak Fen

R.A. Zielinski

Core samples of as much as 3.6 m of reed-sedge peat and 3 m of underlying organic-rich lake sediments indicate the distribution of uranium (U) as a function of depth in a U-enriched fen, north-central Colorado. Cores with generally high concentrations of U (100 to 3000 ppm in most 0.3-m intervals) are located close to identified point sources of uraniferous ground water. Depth-related variations of U within each core are strongly influenced by vertical differences in hydraulic conductivity, which determine the flux of dissolved U to a particular interval. Additional controls on U concentration include: (1) the abundance and surface area of sorbant organic matter, (2) the paucity of dissolved complexing agents (carbonate, phosphate) that would otherwise stabilize U in solution as uranium-VI species, and (3) depth-related decreases in Eh that may promote eventual reduction of some sorbed uranium-VI to relatively insoluble uranium-IV species. Fluctuation of the water table and bacterially mediated generation of H_2S are two probable causes of Eh variations.

The Use of Radon-222 as an Indicator of Ground Water Input and for Flow-rate Determination at Boston Peak Fen

D.E. Owen

Radon-222 (Rn), a naturally occurring radionuclide (part of the Uranium-238 decay series), is found in detectable amounts in most ground water. Rn can readily be separated from water samples in the field and measured in an alpha scintillation counter. Because Rn has a half life of 3.8 days, it makes an excellent indicator of recent minerotrophic water input. After 15 days, only 6% of the original Rn concentration remains. Therefore, Rn can be used to determine whether pools present in a wetland have a strong connection to the ground-water system or are being fed by waters moving slowly through the peat. Radon can also be used as a natural tracer to determine the flow rate of water from point sources, such as spring pools. The test procedure involves digging small pits at regular intervals away from the spring pool and leaving them undisturbed for at least 26 days, before measuring their water Rn concentration. The decay curve of Rn is used in conjunction with the spring pool (source) Rn concentration, to calculate a flow rate from the point source. I calculated flow rates between 4.5 and 5.2 cm/day for water movement from several spring pools in the Boston Peak fen.