PROCEEDINGS OF A U.S. GEOLOGICAL SURVEY WORKSHOP ON ENVIRONMENTAL GEOCHEMISTRY

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Edited by BRUCE R. DOE

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PREFACE

Environmental geochemistry encompasses both natural chemical (geochemical) hazards and anthropogenic environmental concerns. For example, the household radon contamination that generated so much public awareness in 1986 can be considered a natural radiochemical hazard except in those cases involving mine tailings from uranium and phosphate deposits. The radon emanates through natural processes dependent upon the abundance of radioactive parents of radon (most significantly ^{238}U and ^{326}Ra) and the permeability of the rock or soil upon which a house is built. On the other hand, the effects of chemical waste disposal (for example, dioxin) are an anthropogenically induced concern. Some contamination problems can be extremely complex and involve a combination of both natural and anthropogenic causes. The selenium problem at the Kesterson Reservoir in the western San Joaquin Valley of California, for example, seems to involve concentration of naturally occurring selenium as a result of irrigation practices. The quality of our drinking water also depends on both natural and anthropogenic factors.

When an environmental geochemical problem arises, the public expects a rapid response from scientists and organizations. To help prepare for possible future concerns, the U.S. Geological Survey held a workshop in April 1986 to determine what sorts of studies have been completed or are in progress and to generate some ideas regarding future studies. This circular summarizes the proceedings of that workshop and provides a sampling of the kinds of investigations the U.S. Geological Survey is prepared to do. This circular is not an exhaustive compendium. For those desiring greater detail, reference can be made to publications listed in the bibliography by Shacklette and colleagues (this volume).

The U.S. Geological Survey often can quickly reorder priorities to encompass newly recognized societal concerns. In the case of environmental geochemistry, two examples of rapid reprogramming are discussed in included papers and are briefly described here. Gundersen (this volume) was conducting field-geochemical uranium-resource studies in the Reading Prong of Pennsylvania, New York, and New Jersey when the household radon issue surfaced in the now famous Watras house early in 1985. She was able to rapidly alter her course of mapping from emphasis on uranium resource to radon environmental geochemistry. In another example, when the selenium concern arose at the Kesterson Reservoir in California (overview by Sylvester, this volume), Tidball and colleagues (this volume) were able to draw on a suite of samples previously collected and analyzed for reconnaissance mineral-resource evaluation and low-density geochemical mapping purposes. Because of the reconnaissance nature of the original study, the simple, rapid analytical technique used was not extremely precise and did not measure selenium, arsenic, and mercury. Therefore, Tidball and colleagues reanalyzed the samples by more precise means and added the toxic elements to the suite. This reanalysis enabled them to rapidly develop the soil trace-element distribution maps that identify the area in the vicinity of the Panoche-Cantus Creek fans in western Fresno County as being the selenium-enriched source area (described more fully by Presser (this volume)). A more thorough discussion of selenium in the West is given by McNeal and colleagues. Soils are especially important in environmental geochemistry investigations, and so thorough attention is given to them (for example, papers by Tidball, by Pavich, and by McNeal), as well as to various aspects of bedrocks (papers by Conner, by Hearn and colleagues, by Orem, and by Kotra).

Concerns involve not only toxic levels of elements and compounds but also deficiencies of essential elements. Selenium, for example, is needed in human and animal diets. Indeed, in the eastern San Joaquin Valley, some fields are doped with selenium to provide grazing animals with adequate amounts of this element in their diets. The diet of most Americans is sufficiently varied so that getting adequate selenium is not an issue. Plant geochemistry, in general, plays a major role in environmental studies, however, beyond providing nutritional information and thus is broadly discussed herein (by Erdman, by Milton, and by Gough and colleagues).

The techniques used in environmental geochemistry are not confined to chemical analyses or geologic field mapping. Duval (this volume) applies aerial gamma-ray data gathered by the U.S. Department of Energy's National Uranium Resource Evaluation Program (NURE) to the household radon issue. Thus, this investigation uses data gathered for a purpose not originally intended, as in the case of the San Joaquin Valley. ^{214}Bi is a decay product of ^{222}Rn in the radioactive decay chain of ^{238}U and is the radioisotope actually measured; thus the NURE data are directly applied to radon concerns. Several papers explore the applicability of other geophysical techniques to environmental geochemistry (for example, papers by Frischknecht and by Clark and King). Various kinds of electrical property measurements appear to be particularly appropriate (papers by Olhoeft and by Bisdorf). Unique properties of asbestos varieties require detailed mineralogical studies (paper by Ross). Stable and radioactive isotopes also have considerable application (papers by Spiker and by Muhs and colleagues, respectively).

Perhaps most,if not all, of the Nation's estuaries are suffering from pollution effects. (Examples of concerns in Massachusetts are given in two papers by Bothner and another by Butman.) Subsurface problems associated with estuaries are discussed by Helley, and Butman discusses offshore aspects. Manheim discusses some possible consequences of submarine mining.

Although this circular gives an impressive sampling of efforts and capabilities of the U.S. Geological Survey in environmental geochemistry, it is by no means comprehensive. Only the most timely topics are emphasized herein. Unaddressed are issues relating to major elements that pose potential hazards, such as aluminum and magnesium, and numerous minor elements (for example, arsenic, barium, cadmium, lead, mercury, and zinc). It is also recognized in light of the experience at the Kesterson Reservoir, Calif., where samples collected for resource purposes allowed rapid response to an environmental concern, that data collected for purposes of resource exploration geochemistry can have considerable application to future environmental concerns. Society's concern over environmental geochemistry does not seem to abate. Each year seems to bring a new issue. In spite of this happening, only one State, Missouri, has complete coverage of environmental data in even a preliminary fashion (see papers by Shacklette, by Miesch, and by Erdman and letter by Howe). Organization within the U.S. Geological Survey to address these problems seems appropriate. A first step was the initiation of the Toxic Substances Hydrology Program (see Mallard and Ragone, this volume). Initial planning on a possible program involving solid materials has been outlined by Filipek. Consideration is being given to a comprehensive overall plan.

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By Lorraine H. Filipek

INTRODUCTION

Issues and Problems

Taken collectively, environmental issues have become one of the most visible concerns of the American public for several decades. Every few months a new environmental problem surfaces. High selenium concentrations at the Kesterson Reservoir in the San Joaquin Valley are causing death and deformities in wildlife. Acid rain is degrading water quality in eastern lakes. Indoor radon pollution may increase risk of lung cancer and is being discovered in new areas daily, including major population centers like Washington, D.C., and Philadelphia. Soil erosion is seriously reducing the amount and quality of our Nation's and the world's topsoil.

The combined cost of these problems is tremendous in terms of both dollars and quality of life. For example, the Federal Government has already spent several million dollars trying to correct the Kesterson selenium problem, and the Office of Technology Assessment recently estimated that it could cost as much as $100 billion to clean up the more than 10,000 hazardous waste sites that pose a serious threat to public health (Magnuson, 1985). Remedial actions such as these are orders of magnitude more expensive than prior scientific assessment and proper preventive measures. The Committee on Irrigation-Induced Water Quality Problems of the National Research Council (NRC) pointed out in its review (Eliot, 1985, p. 921) of the Bureau of Reclamation's San Joaquin Valley Drainage Program, "Failure to assess the problem explicitly in advance wastes time and multiplies effort. This appears to be happening to a degree in the San Joaquin drainage (selenium) studies." The San Joaquin study was singled out by the NRC, but the statement applies in general to environmental problems because there is no systematic environmental assessment strategy in the United States. Moreover, no such strategy can exist until we have a better understanding of the surficial Earth.

The Earth functions as an interactive system of land, water, air, and biota. Physical, chemical, and biological processes occurring at and near the Earth's surface are important in all of the previously mentioned environmental issues. Naturally occurring selenium, weathered from nearby mountains, is transported to soils and concentrated in drainage water from crop irrigation in the west side of the San Joaquin Valley. The effects of acid rain depend upon the ability of the local soils and rocks to neutralize the acidity. The radon gas invading homes is a natural product of the radioactive decay of uranium and is concentrated through complex interplay among bedrock, soils, the atmosphere, and house construction. Rates of agriculture-induced soil erosion depend on the local geomorphology.

It is becoming increasingly evident that we live in an environment that has important, but generally poorly known, broad-scale variations. In a manner similar to regional topographic variations, geochemical processes and concentrations show important regional differences. The natural causes of some of these variations are at least partially understood. For example, the mobility of anionic species such as selenium, arsenic, uranium, and boron is much higher in the alkaline, saline soils and waters of the arid Western United States than in the acidic soils of much of the humid East, whereas cations such as lead, zinc, cadmium, and iron are more mobile in acidic environments. For the most part, however, the causes and extent of regional variations and the resulting variable impact of human activities are not clear.

The U.S. Geological Survey (USGS) has several programs that provide much needed data on regional water quality and hydrology. But water is only one component of the surficial Earth system. The quality of surface and ground water is a function of the geochemistry and geomorphology of the land—the sediments, soils, and rocks—over and through which the water moves. The land plays several roles. It may act as a "filter" or sink, stripping water of human and natural contaminants; as a natural source of contamination due to high concentrations of potentially toxic elements associated with mineral deposits; or first as sink and then as source responding to changes in human activities, such as building or draining a reservoir. The actual earth materials themselves, eroding at accelerated

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rates due to human activities, cause surface-water quality problems due to their sheer volume.

Thus, to determine which natural and human factors control our surficial environment, we must understand the interactions among land, water, air, and biota. However, present information is limited on both (1) the concentrations of naturally occurring toxic or nutrient elements in the soils and rocks of the highly complex and variable natural geologic environment and (2) the types and rates of processes involved in the redistribution of elements and surficial materials under different geologic and climatic regimes (weathering and erosion). Problem-specific programs such as those related to acid rain or toxic wastes have been funded to investigate various individual environmental issues. However, there is as yet no truly integrated approach to the study of the surficial-Earth system. Geologic, geochemical, and geophysical data on earth materials and weathering-process studies that span the climatic and geologic extremes of the Nation are needed to develop systematic environmental assessment and mitigation strategies. Such strategies are needed if we are to recognize and effectively solve present and unforeseen environmental problems, or better yet, to prevent them from arising at all.

The timing for the Environmental Geochemistry Program is right. We have not only the need, but also the technical and knowledge base to make great progress in understanding the various surficial processes and incorporating that understanding into effective strategies to protect the Earth from irreversible degradation. With the Environmental Geochemistry Program, geochemical data and process-related information on bedrock and erosion products will be collected to provide the framework for understanding and interpreting the physical, chemical, and biological characteristics of the land-surface environment. In addition, the understanding gained about the functioning of the surficial Earth will be incorporated into systematic environmental assessment strategies to protect our Nation's and the Earth's environmental health.

Justification for U.S. Geological Survey Action

The USGS was established as a scientific agency to provide information about the Earth for use in reaching informed decisions related to national needs. The quality of the environment is one of the most important and publicized national and international concerns of our time. It is also one that invokes extremely emotional debate. The issues involved are scientifically complex, and there is inadequate understanding of the causes and of the effectiveness of the proposed solutions. The cost of environmental problems in lawsuits alone is immense, not to mention the cost of cleanup or mitigation, which in many cases is inadequate or ineffective. The USGS is national in scope and has a reputation for being an impartial scientific agency responsible for information on earth-science issues. Therefore, data and assessments presented by the USGS are likely to be viewed as objective by all interested parties.

The USGS is investigating the quantity and quality of the Nation's waters, with topographic and geographic information system (GIS) input and coordination with other agencies. These efforts will constitute the Nation's first fully integrated investigation of the surficial Earth environment. The complementary USGS Environmental Geochemistry Program is needed to (1) compile existing geoscience data and build new data bases about the materials that make up the land surface, including concentrations of rock-forming, toxic, and nutrient elements and their relation to geologic and geomorphic features; (2) gain an understanding of weathering and erosion processes affecting the chemical and physical makeup of these surficial materials; and (3) integrate the data bases and process-oriented research into coherent strategies to assess the environmental quality of the Nation.

Collection of geochemical and geomorphic data on solid earth materials and investigation of the physical, chemical, and biological processes occurring at and near the land surface are necessary to provide appropriate mitigation strategies to reduce present environmental contamination or degradation (or know when mitigation is unfeasible given the geologic constraints). Further, development by the USGS of systematic assessment strategies will allow rapid determination by Federal and State agencies of areas that have the greatest present and potential contamination or degradation hazards and will allow development of appropriate land-use strategies to prevent further health hazards and (or) environmental deterioration. Finally, this program will provide an effective, efficient medium for cooperative interaction by the USGS with other international, Federal, and State agencies, universities, and scientific organizations who are interested in particular environmental problems.

PROGRAM DESCRIPTION

Objective

The program objective is to develop an integrated multidisciplinary, or "interdisciplinary," framework within which broad-scale environmental problems can be addressed. This framework will include:

1. Development of a national data base of environmental geochemistry and surficial-Earth parameters that includes concentrations of rock-forming, toxic, and nutrient elements and their relation to geologic, geomorphic, hydrologic, biologic, climatic, and present land-use variables.
2. Research leading to a more quantitative understanding of the physics, chemistry, and biology of weathering and erosion processes and the rates of these processes on spatial scales ranging from molecular to regional and global.

3. Development of optimum environmental assessment strategies and reports in cooperation with other appropriate agencies, focusing first on areas of known immediate risk to health and the environment.
4. Systematic production of scientific reports and of regional and national environmental assessment maps.

Anticipated Benefits of the Program

The anticipated benefits of the program include the following:

1. Evaluation and prediction of areas having environmental contamination or degradation hazards and ability to distinguish between the effects of natural processes and human activities.
2. Establishment of geochemical baselines for solid earth materials against which potential future changes can be assessed.
3. Scientifically based mitigation strategies for reducing contamination and degradation of surficial-Earth materials.
4. Greatly decreased financial and health costs from environmental hazards.

STRATEGY

General Description

We propose to develop an integrated multidisciplinary framework that will allow a systematic assessment of present and potential environmental quality and the factors that control that quality. The Environmental Geochemistry Program will collect geochemical data and process-related information, drawing heavily upon relevant data bases and experiences of previous work. The Environmental Geochemistry Program will be closely coordinated with the National Geologic Mapping, Climate, National Mineral Resource Appraisal, Development of Assessment Techniques, Acid Rain, Toxic Substances Hydrology, Radioactive Waste, and other relevant USGS programs. The combined research and assessment map products of the Environmental Geochemistry, Climate, and other USGS programs will allow Congress; international, Federal, and State agencies; and individuals to develop appropriate strategies to reduce present environmental contamination and degradation and to minimize future problems.

The strategy of the Environmental Geochemistry Program is (1) to investigate broad-scale environmental problems in specific geographic areas (study areas) of various sizes in cooperation with other agencies, (2) to use an integrated multidisciplinary approach that draws upon the full arsenal of relevant USGS expertise, and (3) to extrapolate the resultant information to better understand issues at the regional, national, and global level. Investigations that will be carried out in this program are of two complementary types:

Environment-oriented.—Comprehensive investigations within a single environment, such as determination of the influence of different parent rock types on weathering rates and chemical composition of weathering products within a particular ecoregion and calculation of average regional weathering rates. (An ecoregion is a region having relatively uniform factors that cause and integrate surficial environmental processes, including climate, physiography, potential natural vegetation, soils, and land use (Omernik, 1987, p. 118–125).) This type of investigation has value on several scales. It is useful in isolating areas within the ecoregion that have present or potential environmental problems due to local geochemistry, such as the selenium problem in parts of the San Joaquin Valley, Calif., due to high concentrations of naturally occurring selenium in the soils and ground water of the Panoche Fan. It also provides necessary regional geochemical baseline information for monitoring the effects over time of such broad-scale processes as acid rain and regional or global changes in temperature or ozone.

Issue-oriented.—Statewide and nationwide investigations of a single issue, such as the geologic and geochemical causes of high indoor radon levels in houses, lead or arsenic in soils and drinking water, nitrates in ground water, or cadmium in crops. This type of investigation will incorporate surveys and research at several small study areas in different geologic and climatic settings across the Nation. It will allow rapid national evaluation and prediction of areas having the greatest potential for acute problems.

The environment-oriented and issue-oriented investigations will provide valuable transfer of information to each other in an iterative manner. The priorities for study-area selection will be based on knowledge of potential natural contamination or degradation hazards, on the perceived need for a rapid response, and on the interest and cooperation of other Federal and State agencies. Highest priority will be given to those regions or problems on which several agencies are able to work cooperatively. The study areas will be the focus of activities of the program's five elements:

1. Data management and analysis to determine the availability and quality of existing surficial-Earth data and to integrate the data into a standard format suitable for a national data base of environmental geochemistry and surficial-Earth parameters.
2. Geochemical and geophysical surveys to identify and distinguish between present anthropogenic toxic-element sources and natural sources, such as bedrock, mineralization, and weathering products, and to quantify the degree of natural chemical input to the surficial environment.

3. Interdisciplinary field and laboratory weathering-process research to identify the factors that affect the types and rates of rock-water and rock-air interactions at Earth-surface conditions and to determine transport rates and mechanisms.
4. Methodology research to develop approaches and analytical methods as required to meet other programmatic objectives.
5. Environmental assessment mapping, based on systematic assessment strategies, to allow rapid determination of those areas having the highest present and potential contamination or degradation risks.

Development of the assessment strategy for each environmental problem will be iterative over the generally 4- to 7-year course of a study-area project. In the first and second years, existing data will be compiled, and a set of hypotheses and a preliminary assessment map will be developed. Beginning in the second year and continuing 2 to 5 years, geophysical and geochemical surveys and weathering-process research will be conducted in the study area.

In the final year of field research, the survey and research information will be synthesized into a summary report and a revised environmental assessment map for the area. Generalizations of contamination or degradation processes will be developed on the basis of the new information gained in the study areas, and regional, national, and international assessment maps will be developed as appropriate.

Program Elements

Data Management and Analysis

Many studies have already been done on various aspects of the surficial Earth. This information is scattered throughout the literature and at various Federal and State agencies, universities, and private repositories. Before any field work is started at a particular study area, the relevant existing data will be assembled, organized, and put into a standard format suitable for a national data base of environmental geochemistry and surficial-Earth parameters. Study-area maps will be compiled of geology, topography, soil properties, geophysical features, vegetation, hydrology, and land use, by using GIS technology. When applicable, a statistically determined subset of National Uranium Resource Evaluation (NURE) stream sediment samples will be analyzed statistically or reanalyzed chemically for elements of interest. For radon, aeroradiometric geophysical maps derived from the NURE data base will be generated. Geological maps will be compiled cooperatively by the USGS and the relevant State survey, usually as part of the National Geologic Mapping Program. The USGS will compile hydrologic maps that have been developed through its various programs. The other maps will be developed cooperatively by the USGS and other appropriate agencies. The final products will be prepared by the USGS.

Geochemical and Geophysical Surveys

The geochemical and geophysical surveys will provide new baseline data on the materials that make up the surface and near-surface environment. Together with the maps prepared in the first program element, they will provide the context within which the process-oriented field work will be accomplished.

Geochemical surveys will focus on the production of statistically stable (reproducible) geochemical maps and data bases for each element of interest in each geochemical medium appropriate to the study area, including soil, rock, stream sediment, surface and (or) ground water, and vegetation. These baseline data are important because they indicate what is "normal" in any particular area and provide the background context within which problems can be identified. Geochemical maps have already proven extremely useful in identifying potential problem areas, such as the source area for the elevated selenium concentrations at the Kesterson Reservoir in the San Joaquin Valley. Existing geochemical information generally will be compiled for the study area in the year preceding initiation of the geochemical survey to aid in selection of the most appropriate sample media. The actual sampling scheme will be designed to suit the needs of the particular study area. Before the onset of the first survey, a quality-assurance program and quality-control procedures will be instituted for the collection, preservation, storage, and analysis of all samples.

Geophysical surveys will focus on development of the physical framework of the surface and subsurface using remote-sensing techniques. Broad-scale satellite and airborne surveys will provide the regional framework, and detailed ground-based surveys will outline specific problem areas. Spectral techniques will be used to map vegetation and areas of vegetation stress. Various electrical, electromagnetic, seismic, and radar techniques will be used to map stratigraphy, water table, aquifer boundaries, rainfall wetting fronts, and contaminant plumes, where appropriate.

Weathering Process Research

Weathering process research will be designed to gain a quantitative understanding of the types and rates of interaction among surficial-Earth parameters, such as bedrock geology and geochemistry, geomorphology, soil properties, biology, hydrology, climate, and land use, and the sensitivity of these interactions to change. Integration of an understanding of modern processes with knowledge of the Quaternary geologic record will allow effective use of the geologic record to determine the relation between frequency and magnitude of geologic events and to establish a predictive capability. The focus of research will vary with the particular study area, but the approach will always be interdisciplinary, with synthesis of the results that will allow extrapolations to similar situations elsewhere in a national and global context. The understanding gained will enable international, Federal, and State agencies and individuals to develop effective, scientifically based mitigation strategies to combat contamination or degradation problems. Four major activities will be carried out in this element.

1. Detailed investigations of rock, soil, water, plant, and microbe interactions for different lithologies within a single ecoregion or geomorphic unit to determine (a) the effect of different rock chemistries on rates of weathering and erosion within an area of relatively uniform external environmental variables, (b) the effect of geomorphology on the types and rates of weathering of the parent rock and erosion of the associated soil, (c) the geochemical forms of the major and trace elements in the soils and waters from selected sites within the study areas, and (d) the cause-and-effect relations of geochemistry and geomorphology to the plant and soil-microbe communities. The mineralogy, geochemistry, and paragenesis of the soils will be determined. Biological research will aim at a better characterization of the relation between biota and the geochemistry of the associated soils.

2. Investigations of the geochemistry and transport of naturally occurring source materials to determine the contribution of natural systems to toxic and radioactive elements in surface and ground water and soil gas, where applicable. These studies will allow separation of natural and anthropogenic sources and will aid in determining the feasibility of various mitigation strategies. The objective of this research will be to determine the geochemistry and transport of toxic elements in and around a range of mineralized systems and problem source rocks in the study areas or similar environments elsewhere. Research will include the determination of (a) the geochemical processes active at the rock-water or rock-air interface; (b) the effects of climate, geomorphology, and bedrock geology on the rates of toxic-element weathering and transport; (c) the geochemical and physical changes that occur to the soil and rock as they are transported to and enter the stream environment; (d) the seasonal variations in soils, stream sediments, and waters; and (e) the ultimate sinks for the toxic elements.

3. Investigations of organic-inorganic interactions to determine the nature and extent of toxic inorganic element associations with organic compounds in the surficial and near-surface environment. Studies will be both field and laboratory oriented. They will include investigations of (a) the effects of environmental variables such as Eh (oxidation potential) and pH on the ability of organic compounds to sorb trace elements, (b) the effect of organic sorption onto inorganic particles, such as clays and oxides, on the particle's cation exchange capacity and ability to sorb trace elements, and (c) the effects of degradation of organic contaminants on the mobility of toxic inorganics.

4. Investigations of the geochronology of weathering processes to determine temporal variations in process rates and to assess the effects of past Quaternary climates on the rates and types of soil formation. Evidence suggests that soil formation in some environments is a series of step-functions rather than a continuous process. However, our knowledge of the thresholds that trigger change is very limited. This knowledge is essential to understanding the consequences of soil degradation and processes of soil formation and regeneration. A major aspect of this activity will be the use of Quaternary dating techniques to correlate synchronous events and calibrate time sequences.

Methodology Research

The research will consist of developing and improving techniques of geochemical, geophysical, biological, and computer analysis needed to carry out the goals of the program. The research on geochemical analysis will focus on (1) the development of new techniques to investigate the surface properties of solid-earth materials; (2) the identification and quantification of the complex chemical forms of oxide-forming and toxic elements in the surficial environment; (3) the development of fast, inexpensive, and accurate techniques for the determination of trace concentrations of naturally occurring toxic elements in solid-earth materials; and (4) the development and improvement of techniques used for concentrating trace elements in water and soil extracts. A critical requirement for surface-property investigations is the purchase of a major piece of analytical instrumentation with which to "see" the surface layer, such as an X-ray photoelectron spectrophotometer or an Auger electron spectrophotometer.

Geophysical research will be conducted to refine indirect detection and measurement techniques, such as electrical techniques for detection of contaminant plumes and processes, and other remote-sensing techniques for identifying such features as stressed vegetation and mineral distributions. Biological research will aim at better determination of "indicator" plants and microbes used as chemical monitors of stressed soil environments. The research on computer analysis will address the GIS technology that will be used to manipulate, integrate, and analyze the large data sets created and also will focus on such problems as correcting for the inconsistencies of NURE aeroradiometric data.

Environmental Assessment Mapping

Efforts will focus on (1) statistical determination of the relations among elements and between element concentrations and geology, geomorphology, ecoregion zone, soil properties, biology, hydrology, and land use; (2) development of environmental assessment strategies based on integration of the statistical interrelations and the process-oriented research; and (3) systematic production of study area, regional, and national environmental assessment maps of surficial-earth materials.

The preliminary regional or national assessment map for any particular toxic element will be formulated on the basis of existing geochemical data and information about mineral deposit districts, geology, ecoregion zone, hydrology, and land use. A scoring technique will be developed similar to that used in mineral-resource assessment. Research in computer analysis technology and expert systems will guide formulation of later environmental assessment maps.

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2. Toxic Substances Hydrology—Surface- and Ground-Water Contamination

By Gail E. Mallard *and* Stephen E. Ragone

INTRODUCTION

Contamination of the Nation's ground and surface waters by toxic wastes is considered by many to be one of the most significant environmental issues of the decade. Billions of gallons of contaminated liquids are discharged into the environment each year (Miller, 1980), and virtually all States have some ground- and surface-water problems resulting from toxic organic chemicals or heavy metals (U.S. Geological Survey, 1984). The extent of the problem, with regard to the percentage of ground water and surface water affected, is not clearly defined. However, problems such as those encountered at Love Canal, N.Y., have focused public attention on the extensive social and economic impact that can result from even a relatively small area of ground-water contamination. As with ground-water contamination, awareness of the seriousness of surface-water and sediment contamination by hazardous substances has increased dramatically in recent years. Conditions such as the occurrence of dioxins at Times Beach, Mo., kepone in the lower James River, Va., and polychlorinated biphenyls (PCB's) in the Hudson River, N.Y., sediment and water have received widespread attention from Federal, State, and local agencies and the general public.

Successful implementation of laws and regulations to reduce environmental degradation from toxic waste contamination requires earth-sciences information. The U.S. Geological Survey's (USGS) Toxic Substances Hydrology Program fulfills an important role in identifying the extent of these problems and providing earth-sciences information needed to improve waste-disposal practices and to help mitigate existing and future surface- and ground-water contamination problems. The program supports studies to (1) develop new and refine existing methods of sampling and measuring hazardous substances in ground and surface waters, aquifer and sediment materials, and biota and (2) acquire a greater understanding of the biological, physical, geological, and chemical processes and other factors that affect hazardous substances in ground- and surface-water systems. This information is necessary to appraise the occurrence, movement, and fate of hazardous substances in the Nation's ground and surface waters and sediments and to determine how these are changing with time.

The program has three major goals: (1) to pursue a broad range of fundamental process-oriented research and methods-development efforts related to contamination of both surface and subsurface hydrologic systems; (2) to conduct intensive, interdisciplinary field research of specific surface and ground waters contaminated by selected types of chemicals; and (3) to improve methods for collecting, analyzing, and interpreting hydrochemical information at regional scales to determine the extent and magnitude of contamination. Studies conducted in the program can be divided into three areas—process-oriented research and methods development, focused field investigations and research, and supportive regional investigations.

PROCESS-ORIENTED RESEARCH AND METHODS DEVELOPMENT

This component of the program includes research in the following topical areas:

Ground-water hydrology.—Research is being conducted to provide a quantitative understanding of the flow of water and the transport of its constituents through the subsurface. New mathematical methods are being developed to better explain the mechanisms by which contaminants mix with ground water or are transported through rock fractures and how gaseous or nonwater phase fluids move through the ground.

Erosion and sediment transport.—Many of the toxic substances that are found in rivers are attached to, and transported with, sediment. Conceptual and mathematical models are being adapted or developed to describe the cycle of detachment, movement, and deposition of sediments in river basins.

Inorganic and organic geochemistry.—The movement of inorganic and organic contaminants may be affected by a variety of reversible or irreversible chemical reactions such as ion exchange, mineral solution or precipitation, ion filtration, absorption or desorption, oxidation or

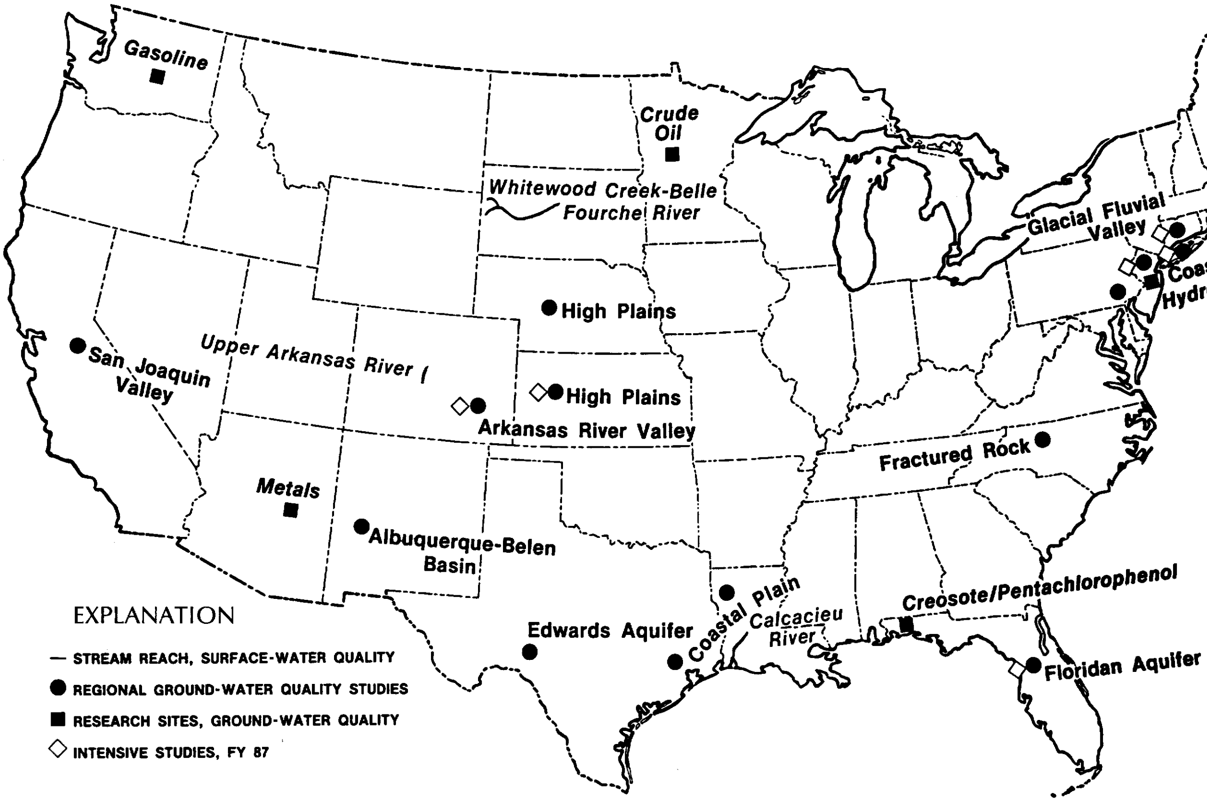

Figure 2.1. Location of U.S. Geological Survey hydrologic studies of toxic substances.

reduction, complexation, and degassing. Research is being conducted to characterize (1) the trace inorganic and organic species found in surface and ground water and (2) the pathways, rates, and controlling factors or reactions of important trace contaminants.

Ecology.—Living organisms accumulate and alter inorganic and organic trace substances. Studies are being conducted to quantitatively relate the concentrations of toxic substances in water and sediment to the concentrations of toxic substances in aquatic biota.

Methods development.—Major research and development are underway to improve methods for sample collection, sample preparation, and analysis for toxic substances. Efforts are being directed toward devising better techniques to obtain representative samples of ground water contaminated by organic chemicals, improving methods for extracting both metals and organic chemicals from solids, and improving the ability to detect and quantify substances present at extremely low concentrations.

FOCUSED FIELD INVESTIGATIONS AND RESEARCH

Field investigations conducted in the Toxic Substances Hydrology Program provide the opportunity to bring together process-oriented and methods-development research in the study of the fate and transport of important types of organic and inorganic contaminants in ground- and surface-water systems (fig. 2.1). In addition to forming a better understanding of earth-sciences processes, the studies allow for the development of new study approaches that can be applied to subsequent studies conducted in the Federal-State Cooperative Program or in other Federally funded programs.

Five interdisciplinary field studies (squares on fig. 2.1) are being conducted to characterize the physical, chemical, and biological processes affecting the fate and transport of trace metals and manmade organic substances in the subsurface. In fiscal year (FY) 1983, studies began at sites where ground-water contamination resulted from a crude-oil pipeline break near Bemidji, Minn., the infiltration of creosote and pentachlorophenol from waste-disposal pits near Pensacola, Fla., and the infiltration of sewage-treatment effluent on Cape Cod, Mass.

Reports describing the studies have been published (Hult, 1984; Mattraw and Franks, 1984; LeBlanc, 1984; and Franks, 1987). In FY 1985, additional sites were selected to study ground-water contamination resulting from chlorinated hydrocarbons at Picatinny Arsenal, N.J., and an acid-contamination plume in Arizona.

Interdisciplinary river-basin investigations are being conducted to describe the occurrence of hazardous substances in water, sediment, and biota and to characterize the fundamental processes that affect these substances in surface waters. Three intensive river-basin investigations (begun in FY 1985 and 1986) are underway and focus on (1) organic chemicals from industrial effluent that is discharged into the Calcasieu River in Louisiana, (2) mine wastes containing high concentrations of arsenic and trace metals that were discharged into the Whitewood Creek and the Belle Fourche River system in South Dakota, and (3) water flowing into the Upper Arkansas River in Colorado from mine drains and abandoned tailings that contributes large amounts of cadmium, copper, iron, and other metals.

SUPPORTIVE REGIONAL INVESTIGATIONS

In FY 1984, the USGS began reconnaissance-phase studies in 14 States (circles on fig. 2.1) in an attempt to test procedures that would systematically evaluate the extent of ground-water contamination. A detailed description of the approach used in the studies has been published (Helsel and Ragone, 1984). Briefly, the objectives of the studies are to systematically collect and use hydrogeologic, land-use, and water-quality data to (1) provide information on ambient ground-water chemistry with emphasis on organic substances and trace metals to explain the chemistry in terms of the local hydrology and human activities and (2) identify the causes, effects, and processes that are applicable to similar areas elsewhere. Study areas range in size from a few hectares to a few thousand square kilometers. Regardless of the scale, each area is characterized by relatively uniform climatic and geohydrologic conditions. The general hydrology and ground-water flow system in the study area are reasonably well understood, and a reasonable body of data is available on inorganic chemical quality of ground water and land use.

The reconnaissance phase of the 14 assessments of ground-water quality in major geohydrologic regions of the Nation was completed in FY 1985. Of the 14 areas (diamonds on fig. 2.1), six were selected for more intensive study.

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3. The State of Soil and Plant Geochemical Surveys

By Hansford T. Shacklette

The application of soil and plant geochemistry to environmental studies requires data on "normal" values in element concentrations to assess changes that have occurred or to predict changes that may occur in the geochemical environment. Data for certain types of natural materials, available from many published reports, may facilitate the planning and execution of a proposed study by providing baseline values for identifying anomalous values in the sampling media. If baseline data are not available, they must be established in the course of the proposed environmental study, thus increasing the cost in time and money for completing the project. It is appropriate, therefore, to review the present state of soil and plant geochemical studies, including available data bases for many elements, before planning future environmental studies.

The data bases already established differ in the objectives for which the data were developed, the chemical elements considered, and the geographical areas studied. For example, for geochemical studies focused on exploration for mineral deposits, only a few chemical elements were analyzed, and the study areas usually were small. These data may be of limited application to some kinds of geochemical studies, or they may be very useful in solving specific environmental problems. Other geochemical studies were centered on specific problems of environmental contamination or on establishing baselines for normal element concentrations in soils and plants or other natural objects. These environmental studies may be separated into two types: (1) topical studies such as point-source emissions (Miesch and Huffman, 1972) and mine-spoil reclamation (Gough and Severson, 1981) and (2) regional studies having as their objective the characterization of geochemical landscapes, often using multimedia sampling, as was done in the study of the western energy region summarized by Ebens and Shacklette (1982) (fig. 3.1) in which geochemical characteristics were evaluated for various sampling materials by, among others, Schultz and others (1980) (rocks); McNeal (1982) (stream sediments); Severson and Tidball (1982) (soils); Erdman and Gough (1982) (plants); and Feder (1982a) (waters). Other regional studies were of soils and plants of the conterminous United States (Shacklette and Boerngen, 1984) (fig. 3.2).

Multielement geochemical studies that are based on smaller geographic scales may include only one type of sampling material, such as big sagebrush in eight western physiographic provinces (Gough and Erdman, 1982) (fig. 3.3) and airborne chemical elements in plants (Shacklette and Connor, 1973; Connor and Shacklette, 1984) (fig. 3.4). Studies at smaller scales may also include many kinds of sampling materials (rocks, residuum, loess, native and cultivated plants, uncultivated and cultivated soils, waters, and so on) from separate locations in the conterminous United States (data summarized in Connor and Shacklette, 1975). Another type of multielement geochemical study may consider only a sampling material of direct economic value, such as the geochemical characterization of fruits and vegetables and their supporting soils from major areas of commercial production (Shacklette, 1980).

Geochemical surveys of areas having political boundaries may be of particular local usefulness and interest, such as the multimedia geochemical survey of the U.S. Geological Survey coordinated with State agencies of Missouri (Erdman and others, 1976a,b; Tidball, 1976, 1984a,b; Connor and Ebens, 1980; Ebens and Connor, 1980; and Feder, 1982b) (fig. 3.5). A geochemical study of Kentucky focused on rock units (Connor, 1975; 1981a–c) and soils and plants (Tidball, 1975). A survey of elements in soils and plants of Alaska has been completed recently (Gough and others, 1984, 1988) (fig. 3.6).

Many references to the abundance of various elements in soils and plants are available in current literature, including general reference books, textbooks, and journal articles (see, for example, Clarke and Washington, 1924; Turekian and Wedepohl, 1961; Vinogradov, 1959; Kovalevskii, 1979; Rose and others, 1979; Davies, 1980; Brooks, 1983; and Kabata-Pendias and Pendias, 1984). These sources are useful in explaining geochemical processes, providing case histories of geochemical projects, and even in giving regional, or worldwide, estimates of the abundance of many elements in a great variety of natural materials. In many of these references, however, important information necessary for judging the reliability of the data is omitted or inadequately explained due to lack of space. To evaluate the usefulness of the grand means, ranges, norms, or baselines of element concentrations, information

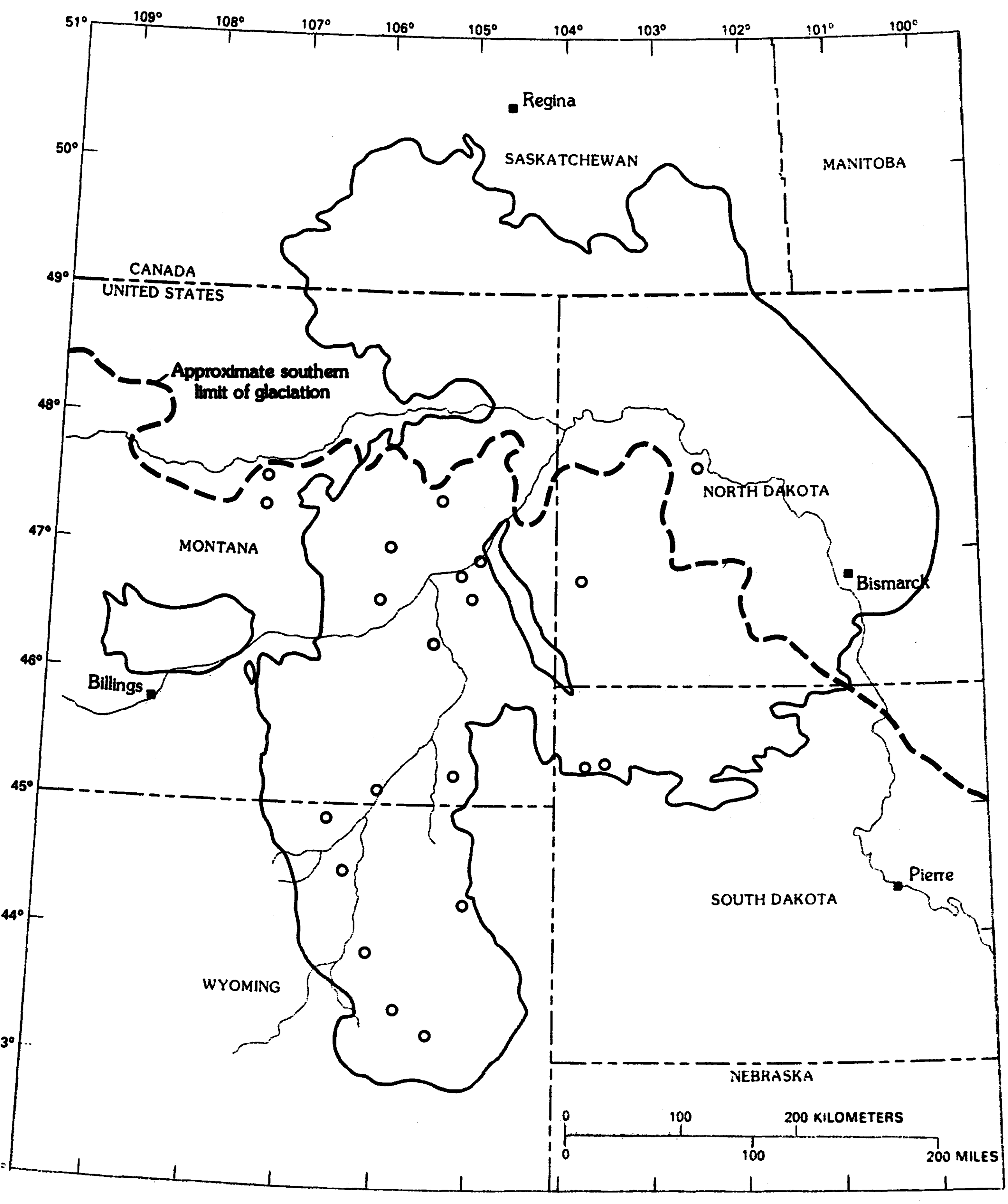

Figure 3.1. Example of a regional geochemical study using various sampling materials. Open circles indicate localities where the A and C horizons of soil, western wheatgrass, silver sagebrush, and above-ground plant biomass were sampled in the northern Great Plains Province. From Ebens and Shacklette (1982).

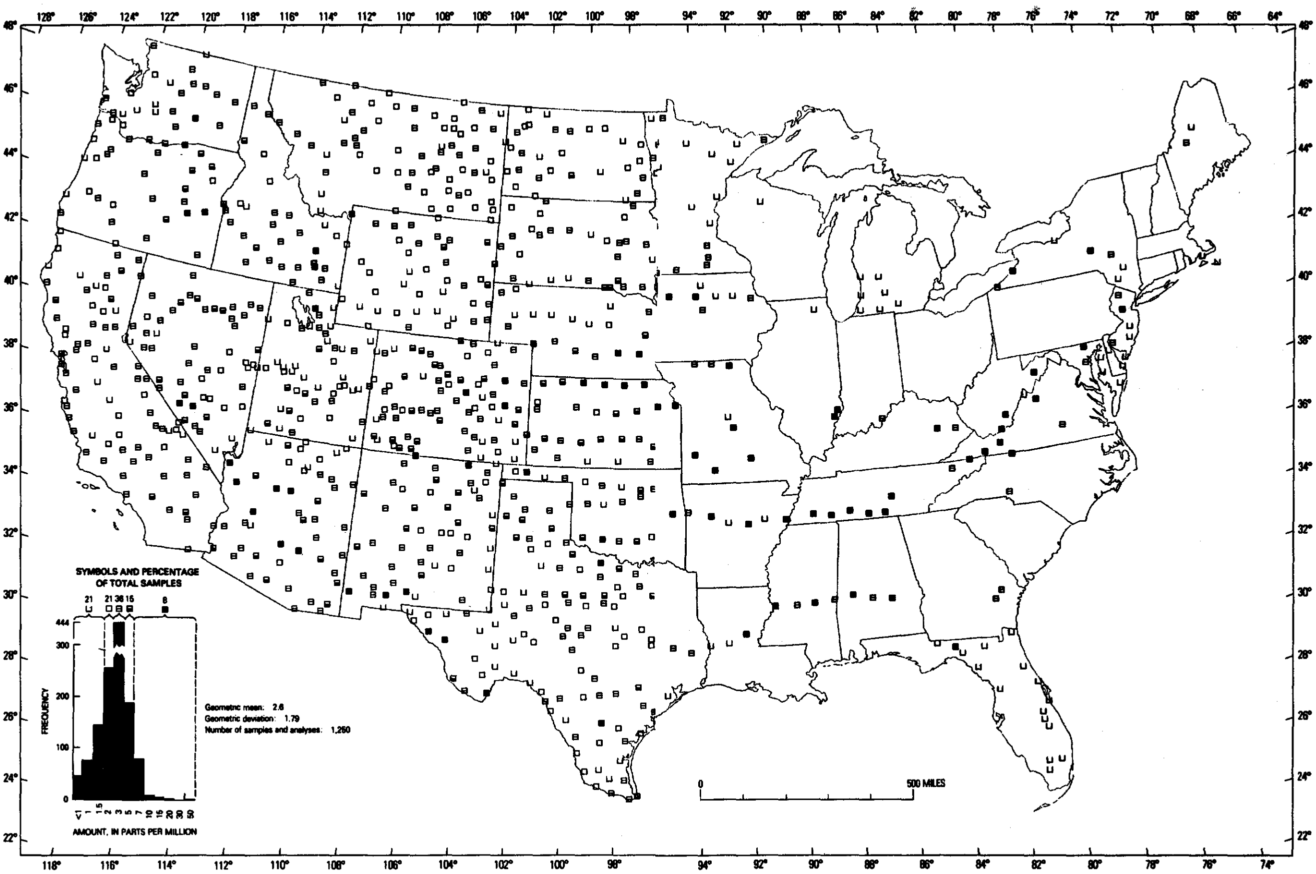

Figure 3.2. Example of a regional geochemical study of soils and plants encompassing the entire conterminous United States—a geochemical study of the broadest scale showing vanadium content of surficial materials. From Shacklette and Boerngen (1984).

on some or all of the following characteristics of the investigation may be essential:

(1) Description of the objectives and areal extent of the study on which the data were based;
(2) Definition of the objectivity of the sampling plan that was used (for reduction of sampling bias, including the basis on which sampling sites were selected);
(3) Adequate descriptions of the sampling media (plant species, soil types or origins, and so on);
(4) Description of the analytical methods used in determining element concentrations in the samples and the sensitivity (limits of quantitative determination) of the methods;
(5) Degree of randomization of the sequence of samples before submission to the analysts, to reduce the effects of error associated with instrumental imprecision and operator bias;
(6) Information on the disposition made of reported element concentrations that were censored (having less than, or greater than, the limits of quantitative determination of the analytical method that was used) and the ratio of the number of samples in which the element was found in measurable concentrations to the number of samples analyzed;
(7) Clear identification of the means and deviations as arithmetic and standard or, preferably, geometric for most elements in soils and plants;
(8) Description of the basis used for the reported analytical values for a sample; that is, wet or dry weight, ash or dried material, extractable or total element concentrations, whole stream sediments or concentrates, and so on; and
(9) Use of analysis of variance methods to determine at what level of the sampling plan (within sites, among sites, among regions) and from what source (sampling or analytical procedures) the greatest and least variances are found. If, for example, an excessive amount of the variance is due to sampling or analytical procedures, reliable estimates of means or baselines for these data cannot be confidently determined.

The term "geochemical baseline" is often used to express an expected range of element concentrations around a mean in a "normal" sampling medium. The baseline would then depend on the limits of the range that are

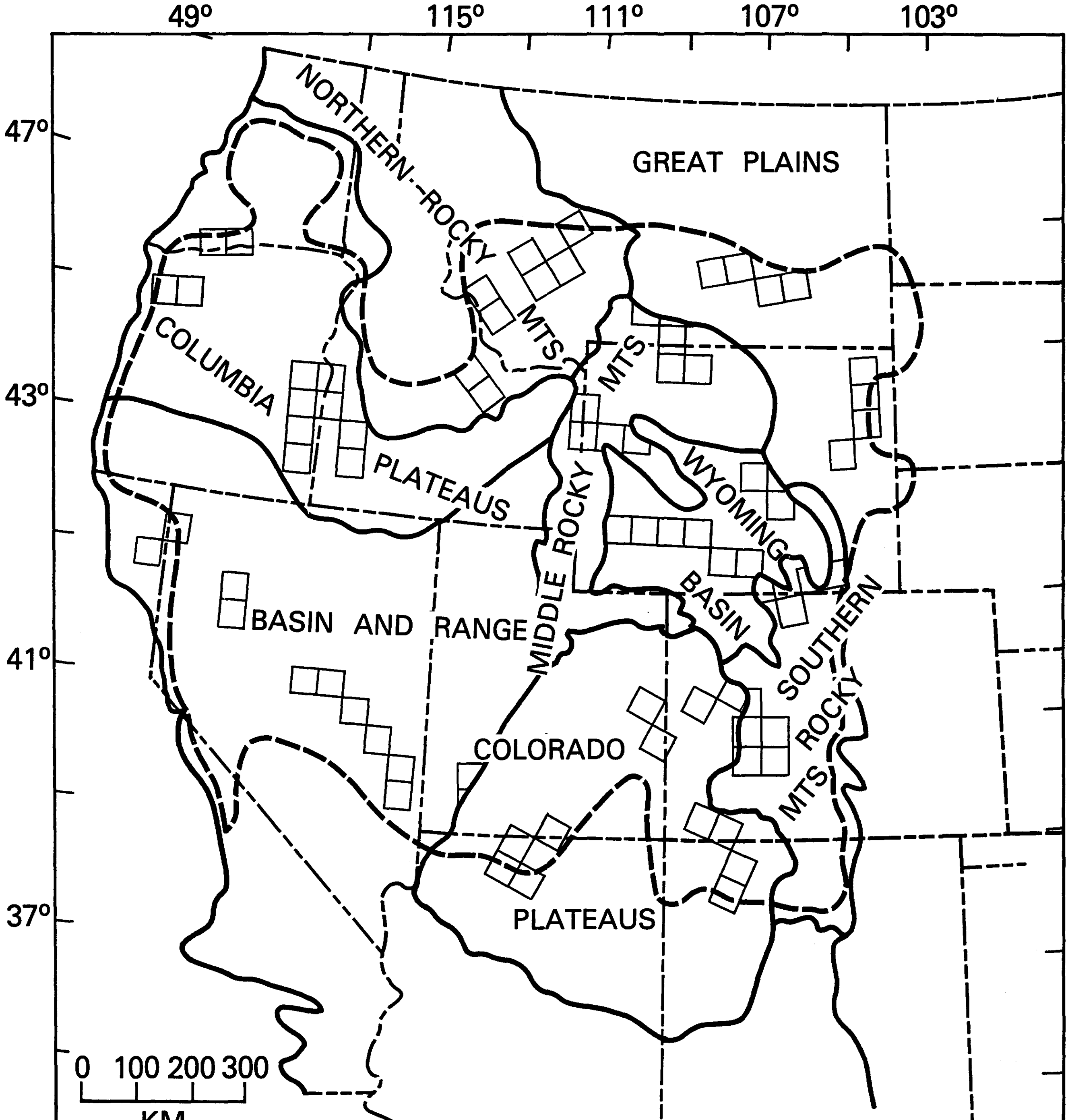

Figure 3.3. Example of a regional geochemical study for one type of sampling material—location of 50-km^2 sampling sites and the general distribution of big sagebrush (bold, dashed lines modified from Beetle, 1960) in eight physiographic provinces (province boundaries after Fenneman, 1931). From Gough and Erdman (1982).

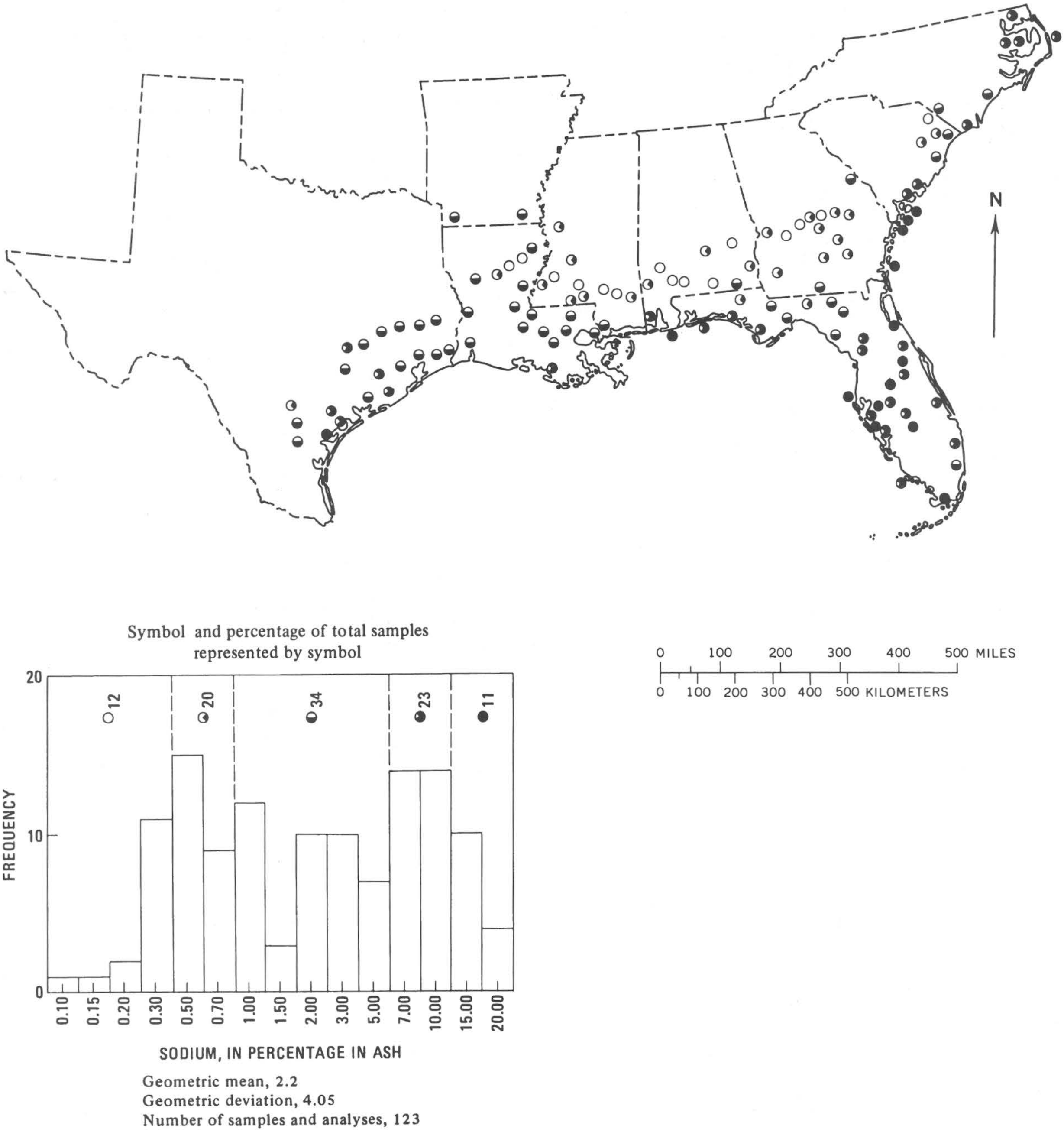

Figure 3.4. Example of a regional geochemical study in which airborne chemical elements in plants are sampled. Symbols indicate sodium content in Spanish moss. From Shacklette and Connor (1973).

chosen. Tidball and Ebens (1976) proposed that, as a reasonable limit on this range, a baseline should encompass the central 95 percent of the observed concentrations because, due to chance alone, samples reflecting natural conditions are expected to fall outside this range only about 5 percent of the time. They stated further that statistical properties of the observed data are more realistic if based on lognormal distribution theory (Miesch, 1976). The expected range may then be expressed as the average of the logarithms ±2 standard deviations of the logarithms. The upper and lower concentration limits of the baseline may be expressed on an arithmetic scale by finding the antilogarithms of the logarithmic limits. The same limits also may be computed for the geometric mean (GM), which is the

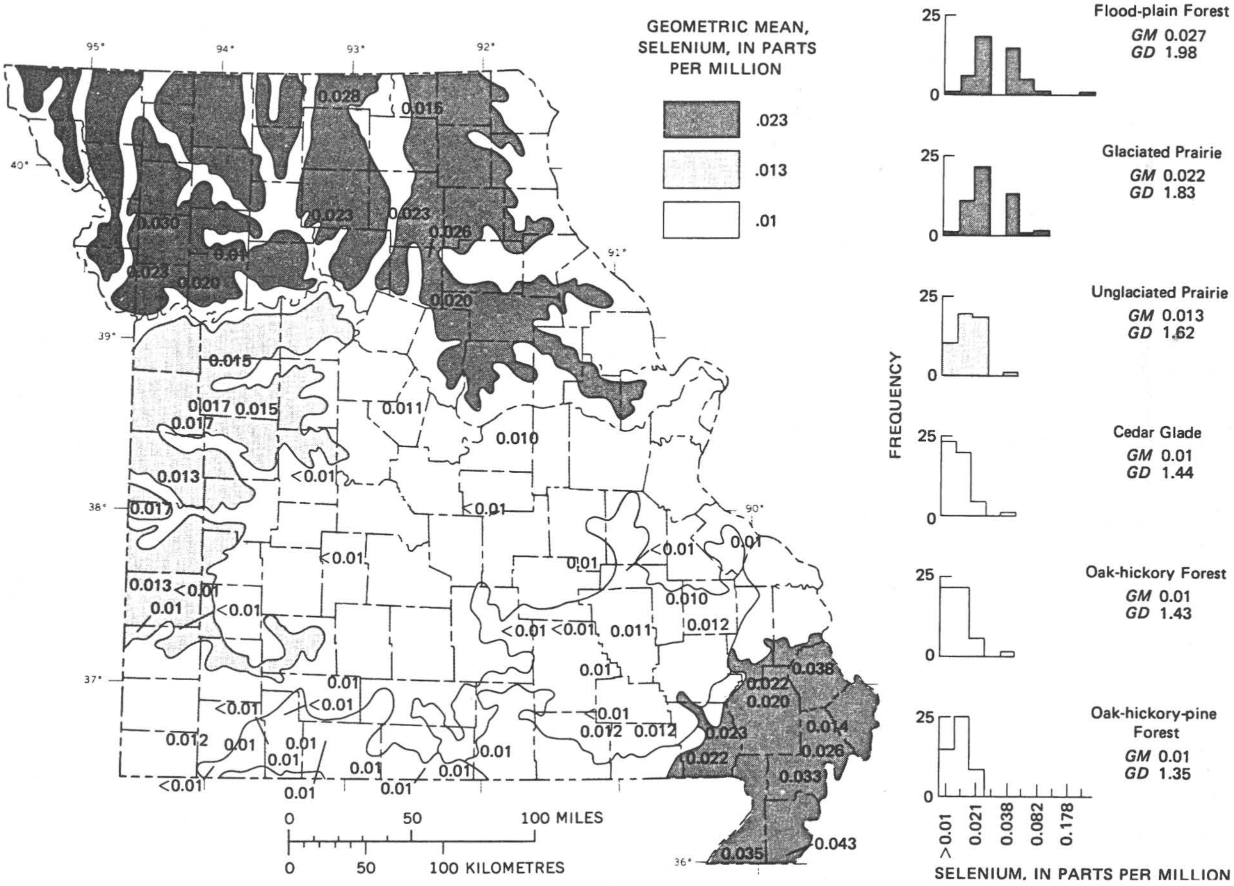

Figure 3.5. Example of a geochemical survey of areas having political boundaries. Vegetation-type areas are classified according to the average concentration of selenium in sumac from Missouri. Each number on the map is the geometric mean concentration of selenium in generally five samples from a 7.5-minute quadrangle. From Erdman and others (1976a).

antilogarithm of the logarithmic mean, and the geometric deviation (GD), which is the antilogarithm of the logarithmic standard deviation. The 95.4-percent expected range lies between $GM/(GD)^2$ and $GM \cdot (GD)^2$. Therefore, to evaluate a proposed baseline for use in geochemical studies of the environment, adequate statistics must be given in a report.

For more than a decade, scientists of the U.S. Geological Survey who specialize in the geochemistry of rocks, soils, and plants, as well as in other natural materials, have conducted environmental studies that complied with all or most of the procedures listed above to provide scientifically defensible geochemical data. These studies, some of which are cited in this report, have been made of areas of many sizes and diverse landscape types where the concentrations of naturally occurring or artificially introduced chemical elements in soils and plants are evaluated. The toxicity levels of many elements to plants, animals, and man also have been reviewed (Gough and others, 1979). These data bases have been developed for soils and plants in environmental studies and probably are unparalleled in scope and reliability. Results of these studies have been presented in U.S. Geological Survey publications, as well as in other scientific journals and books. Many of the reported geochemical data, and some unpublished data, are held in computer files that can be readily accessed.

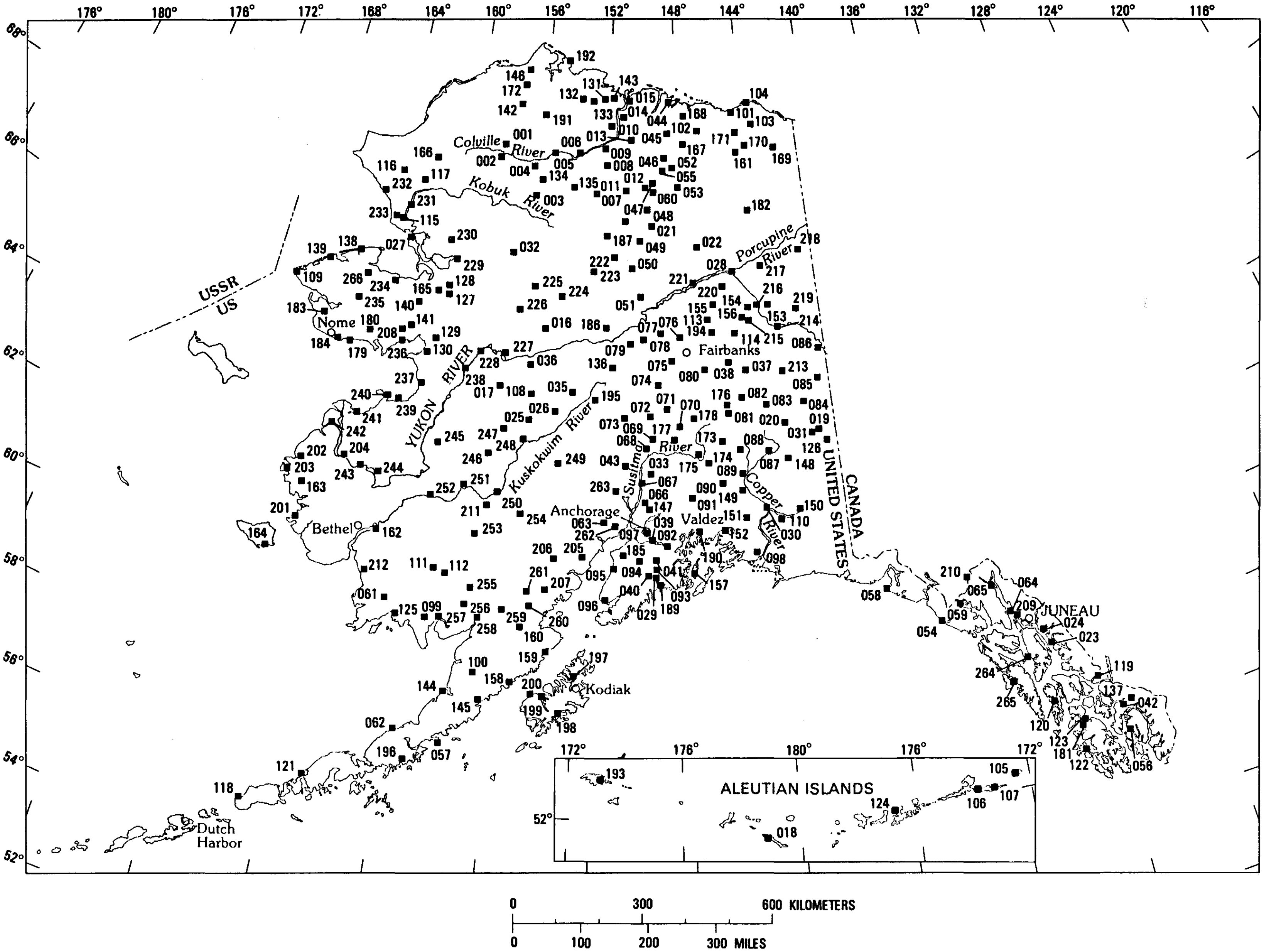

Figure 3.6. Example of a geochemical survey of areas having political boundaries. Solid squares indicate location of sampling sites for soil and plant geochemistry, Alaska. This is a geochemical study of the broadest scale. From Gough and others (1988).

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4. Geochemical Studies—The Missouri Experience

By A.T. Miesch

The field and laboratory methods used in geochemistry by the U.S. Geological Survey (USGS) were developed primarily for mineral-resource assessment programs. As early as 1952, however, a few USGS geochemists and other scientists became involved with problems of geochemistry that were related to human and animal health and with the use of geochemical methods for recognizing and defining environmental pollution. These limited efforts, and the USGS's established leadership in geochemistry, enabled medical scientists and health officials to recognize the potential importance of USGS work in environmental studies. Over the past 30 years, the results of a great many topical studies in geochemistry and health and environmental geochemistry, many done in collaboration with medical researchers, have been published in USGS reports and scientific journals. One of the most extensive efforts in support of medical research was carried out in Missouri.

In 1968, the USGS was approached by the Environmental Health Surveillance Project of the University of Missouri to participate in a cooperative multidisciplinary study of geochemistry and health-disease relations throughout Missouri. The group was led by an epidemiologist and included a health statistician, as well as agriculturists and about a dozen other scientists associated with the university. The basic approach was to accumulate data and compile statewide maps showing variations in health and disease characteristics in both human and animal populations, particularly birth defects in swine. The rationale for studying swine was that more than 3 million piglets were born in Missouri each year, whereas human births numbered no more than 100,000 annually, thus swine provided a much larger sample for statistical purposes. The scientists also showed substantive evidence indicating that health statistics pertaining to swine had a bearing on the human population (Marienfeld, 1972).

The Environmental Health Surveillance Project asked the USGS to design and conduct a program to describe the geochemical variability in the rock substrate, soils and other surficial geologic materials, natural and agricultural vegetation, and ground and surface waters throughout the State. The USGS accepted the challenge not only because of the possibility of lending support to the project, but also because of the opportunity to develop and explore methods for collecting geochemical data specifically for use in epidemiological surveys. Until that time, most of the data collected in health and environmental studies were from small regions and had been meant for very specific purposes. In Missouri, the geochemical landscape was to be described over a broad geologically diverse area in a way that would support not only the ongoing epidemiological studies but also any other environmental investigations that might be conducted in the future. For this purpose, a group composed of three geologists-geochemists, three botanists experienced in field geochemistry, a soil scientist, a hydrologist-geochemist, a statistical clerk, and several part-time personnel was assembled. The group also had the benefit of the USGS's extensive analytical laboratories and experienced analytical chemists, as well as support in computing, library research, technical illustration, and manuscript preparation. Analytical support included truck-mounted field laboratories in a few situations where special onsite analytical work was needed.

There was never a doubt that the USGS team could provide a great deal of geochemical information that could be useful to the Missouri project. As essentially no geochemical information of a regional nature was available, almost any sort of systematic sampling and analytical program conducted on a statewide scope could have yielded useful results. The problem was to make the best possible use of field and laboratory resources in providing the most pertinent geochemical data possible. Because the data were to be examined in relation to data on health and disease, it was also imperative to describe geochemical variations in a manner that was statistically defensible. Statistical defensibility has never been a matter of great concern in geochemistry for mineral exploration because the only geochemical variations likely to be of interest are so large that statistical evaluation is unnecessary. However, it was clear that the magnitudes of geochemical variability that might be related to health abnormalities were almost totally unknown and that small subtle geochemical variations could not be dismissed as unimportant. It was important only that identified variations be real rather than statistical aberrations or at least that the reported variations carry associated levels of confidence or probability. Clearly, the new methods to be used would require heavy use of formal experimental design procedures. To assure that the estimated probabilities were unbiased, it would be necessary to use strict randomization procedures in both the field and laboratory.

The project members, subject matter specialists (geologists, soil scientists, botanists, and hydrologists), were each aware of where to expect the major geochemical variations within the rocks, soils, vegetation, and waters of the State. These variations occur among the major subdivisions recognized within each medium. The major subdivisions in the bedrock, for example, are based on rock type and geologic age; those for soils follow the taxonomic groups of the soil classification system; those for water are based on hydrologic units, and those for vegetation vary according to taxonomy and predefined vegetation-type areas. The first task, one that would yield the most geochemical information the most rapidly and for the lowest cost, was obviously to describe the nature and magnitude of the geochemical differences among these major categories. This task, carried out for each sample medium, was Phase I of a proposed general approach (Connor and others, 1972; Miesch, 1976) to any reconnaissance geochemical survey of this kind. The purpose of Phase I sampling is to define the major geochemical variations associated with the broad regional subdivisions in the material being studied. Phase I sampling may include two stages. Stage 1 consists of preliminary sampling to make estimates of the variations present so that the final sampling in stage 2 can be planned. The estimates of variation are used to select the optimum number of samples in stage 2 for describing as many geochemical differences as possible for any selected level of significance. The general approach is known to statisticians as a two-stage sampling strategy (Stein, 1945). Phase II sampling, in the general approach, consists of sampling to describe geochemical variations within major classifications of the media. It also consists of two stages, one to estimate an efficient sample-spacing interval and another to carry out the final sampling. None of the Missouri work progressed beyond Phase I.

The major results of the geochemical survey of Missouri are published in a series of seven 6-month progress reports issued to the University of Missouri's Environmental Health Surveillance Project (USGS, 1972a–f, 1973) and in USGS Professional Paper 954, which contains chapters on methodology (Miesch, 1976); soils (Tidball, 1976, 1984a,b); natural vegetation, agricultural plants, and associated soils (Erdman and others, 1976a,b); ground and surface water (Feder, 1979); bedrock (Connor and Ebens, 1980); and surficial geologic deposits (Ebens and Connor, 1980).

Support for the USGS's part in the Missouri program waned after it became clear that regional abnormalities in health and disease being sought by the Environmental Health Surveillance Project were more difficult to identify than the geochemical variations. The regional patterns in the health data simply showed no clear relation to the geochemical patterns the USGS had identified. Perhaps no such relations exist, perhaps they are present but extremely subtle, or perhaps the wrong epidemiological or the wrong geochemical data were collected. Nevertheless, the collaborative program between the USGS and the Environmental Health Surveillance Project was a sincere effort and a logical strategy for attacking a problem that is still important. However, no effort such as this can continue very long without the excitement of useful results to encourage its participants and continue the necessary funding.

On the positive side, the State of Missouri has been covered by, at least, the first phase of a statistically sound geochemical survey, and it is the only State so fortunate. The data have already proved useful in helping to resolve several problems in possible metal pollution, some of which are related to waste-disposal practices (Connor and others, 1970; Ebens and others, 1973; Wallace B. Howe, written commun., 1986). It is reasonable to expect many additional uses in the future, as the geochemical maps and other data produced in the Missouri experience will always be there for continuing epidemiological studies.

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5. Written Communication on Environmental Geochemistry in Missouri

By Wallace B. Howe *to* Bruce R. Doe

January 31, 1986

Dr. Bruce Doe
Assistant Chief Geologist
Eastern Region
Geologic Division
U.S. Geological Survey
Reston, VA 22092

Dear Bruce:

I am writing in connection with your phone call and our discussion of January 15th, regarding efforts of the USGS to develop directions in environmental geochemistry. I am also providing a little more information on an attempt we made some years ago to develop interest in a study of natural background radiation levels in the State.

Concerning environmental chemistry first, I have discussed your question with people here, and it is quite clear that there has been more use of the Shacklette and Tidball geochemical survey of the State than I had been aware of or was able to recall in our discussion. Applications of that survey that we are able to identify at this time include the following:

1. Its use in connection with attempts to resolve a case of livestock poisoning by molybdenum in drainage from a strip mine site in Callaway County, Missouri. I believe that this effort actually more or less coincided with some part of the field sampling.
2. A broad characterization of the trace-element distribution in alluvial sediments along the Missouri River and its tributaries in the Kansas City, Missouri, area, where there was a need for background-level information on a number of trace-element occurrences.
3. Its use in providing information on background levels of a number of elements present at the surface in soils and rock in the vicinity of a large hazardous-waste disposal site in Warren County, Missouri.
4. An additional use was the establishment of background levels at several sites where there has been land spreading or irrigation for waste disposal purposes. A specific example is a site where costly, time-consuming litigation was avoided because background information of certain metals was available.
5. There was a section on heavy-metal (Cu, Pb, Zn, and Ba) anomalies in the loess and carbonate residuum in the Washington County area, southeast Missouri, in USGS P954–G (1980), that had implications in the Rolla 2-Degree Project.
6. Its use as reference in *Extraordinary Trace-Element Accumulations in Roadside Cedars near Centerville, Missouri*: USGS P750–B, 1971, p. 1351–1356 (probably from Pb concentrate spills from trucks).

As you know, much effort has been expended on specific geochemical problems concerning contamination. The issues relate to identification of contaminants and potential remedial action. We have been extensively involved in assisting in sampling of innumerable sites in Missouri. However, most, if not all, of the laboratory and related work has been carried out by EPA or through other agencies.

A good case could be made for expanding on the rather broad treatment of Shacklette and Tidball, perhaps focusing on areas that may deserve priority for one reason or another. The long-range objective would be development of more detailed trace-element and other key geochemical background data, in order to 1) demonstrate such an approach at state or regional level and 2) provide greater detail and more in-depth interpretation of the data. If the USGS would be interested in pursuing this general idea, either as a project to be carried out entirely by the USGS or, more desirably from our standpoint, one that we both might approach on a "joint funding" basis, we in the Missouri Department of Natural Resources would certainly like to be informed and would be happy to help in developing a proposal to suit either purpose.

Sincerely yours,

Wallace B. Howe
Assistant Division Director
Division of Geology and Land Survey

6. Soil Studies in the Northern Great Plains

By Ronald R. Tidball

INTRODUCTION

A large area of the northern Great Plains covering parts of four States and Saskatchewan (fig. 6.1) is underlain by large resources of strip-mineable coal. Because of extensive surface disturbance caused by strip mines, contemporary legislation usually requires reclamation of the land surface to a condition that equals or is an improvement on the original condition. This report describes a type of study that has been done in several parts of the northern Great Plains. In each case, the geochemical condition of the soils (that is, total chemical composition) was determined prior to disturbance so that the degree of conformance to future reclamation requirements could be evaluated.

The size of the area studied can cause the magnitude of the sampling task to be overwhelming, particularly if the sampling frequency is high. The sampling task requires an efficient experimental design based on a limited number of samples that provides estimates of the sources and magnitudes of variation, as well as possible estimates of average elemental concentrations in the sampled population.

If a population is homogeneous (has a small amount of natural variation), then only one or a few samples are required to describe that population. If a population is heterogeneous (has a large amount of natural variation), then many samples are required to describe it. In either case, however, sampling error and analytical error must be considered as part of the total variation. We expect the diversity of soils from such a large area as the northern Great Plains coal region to be large. Sources of variation include, but are not limited to, lithology, stratigraphy, climatic zones, vegetation types, soil properties, and degree of soil development. Any prior knowledge that would facilitate subdividing these diverse soils into more homogeneous chemical groups would help to reduce some of the variation and reduce the sampling requirements for estimating stable means. However, if prior knowledge is scarce, estimating as many sources of variation as affordable should be provided for. In addition to defining variation, we also hope to estimate geochemical baselines.

A baseline may be viewed as a collection of data points, each defined as the natural value of a given geochemical measurement in a given sample. Baselines generally are established from data collected from materials confined within an area of interest. However, sometimes extrapolating a geochemical measurement from one area to another is desirable, and this raises the question of how far such a measurement can be extrapolated.

Studies in the Powder River Basin, Wyo. (Tidball and Ebens, 1976; Connor, Keith, and Anderson, 1976), suggest that individual geochemical measurements of soil cannot be extrapolated very far, but that a summary property of a group of samples may be extrapolated over much larger distances depending on the magnitude of the larger scaled features of the variation. The following common geochemical situation in soil studies illustrates how variation affects the ability to extrapolate data.

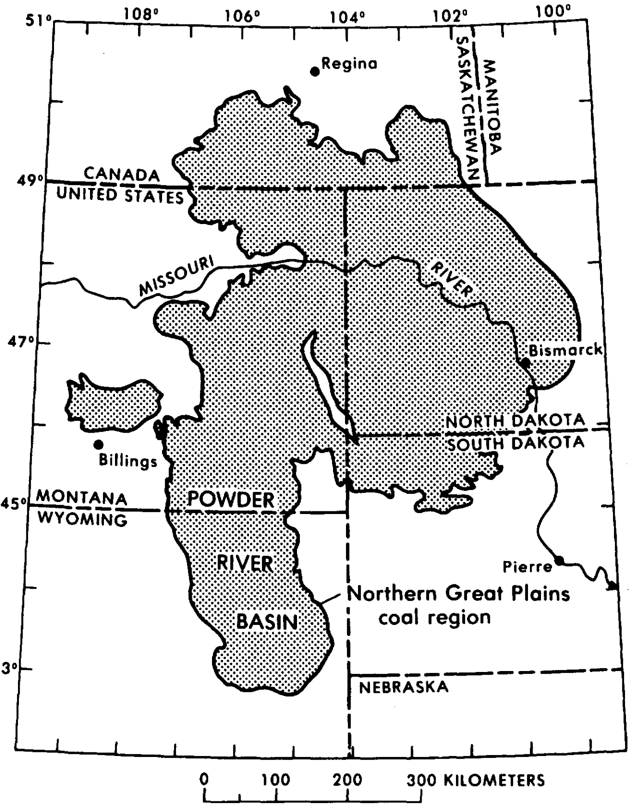


Figure 6.1. Location of the northern Great Plains coal region; area containing coal deposits of Tertiary age indicated by stipple pattern. From Severson and Tidball (1979).

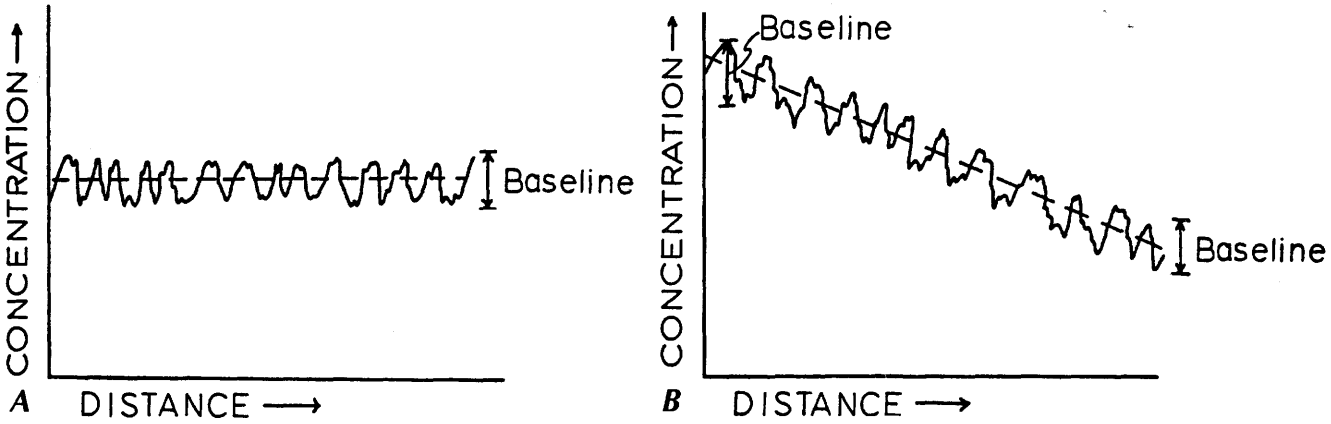


Figure 6.2. Illustrations of hypothetical element distributions along traverses where the regional variation is either absent (*A*) or present (*B*). Baseline is shown as the 95-percent expected range. From Tidball and Ebens (1976).

Assume that the concentration of some element in soil has been measured along two traverses; each element similarly exhibits large changes in concentration from one point to a nearby point (large local variation), but a regional (over larger distances) component of variation is absent at one point (fig. 6.2*A*) and present in the other (fig. 6.2*B*). The large local variation indicates that extrapolation of individual measurements is risky except over very short distances. This inability to extrapolate individual measurements over more than short distances demonstrates the need for some measurement that can be extrapolated. A reasonable range of concentrations (a baseline) defined by the mean and standard deviation is such a measurement. The presence or absence of a regional component of variation, however, is crucial for determining how far the extrapolation may be extended. In the absence of a regional component (fig. 6.2*A*), the distance is large. In the presence of a regional component (fig. 6.2*B*), the distance is limited because of a regional trend; a series of more local baselines would better represent the situation.

DEFINING THE POPULATION

A population of objects or materials that is of interest to us is what we define it to be. The population of soils of the northern Great Plains is defined as the surface horizon of all the natural soils within the bounds of the coal-bearing region that are available for sampling. This is the target population. The set of samples that we collect is the sample population. Inferences about the target population are derived from the sample population. The target population is subject to various sources of variation; once we decide which of these sources can be measured, an appropriate experimental design can be selected.

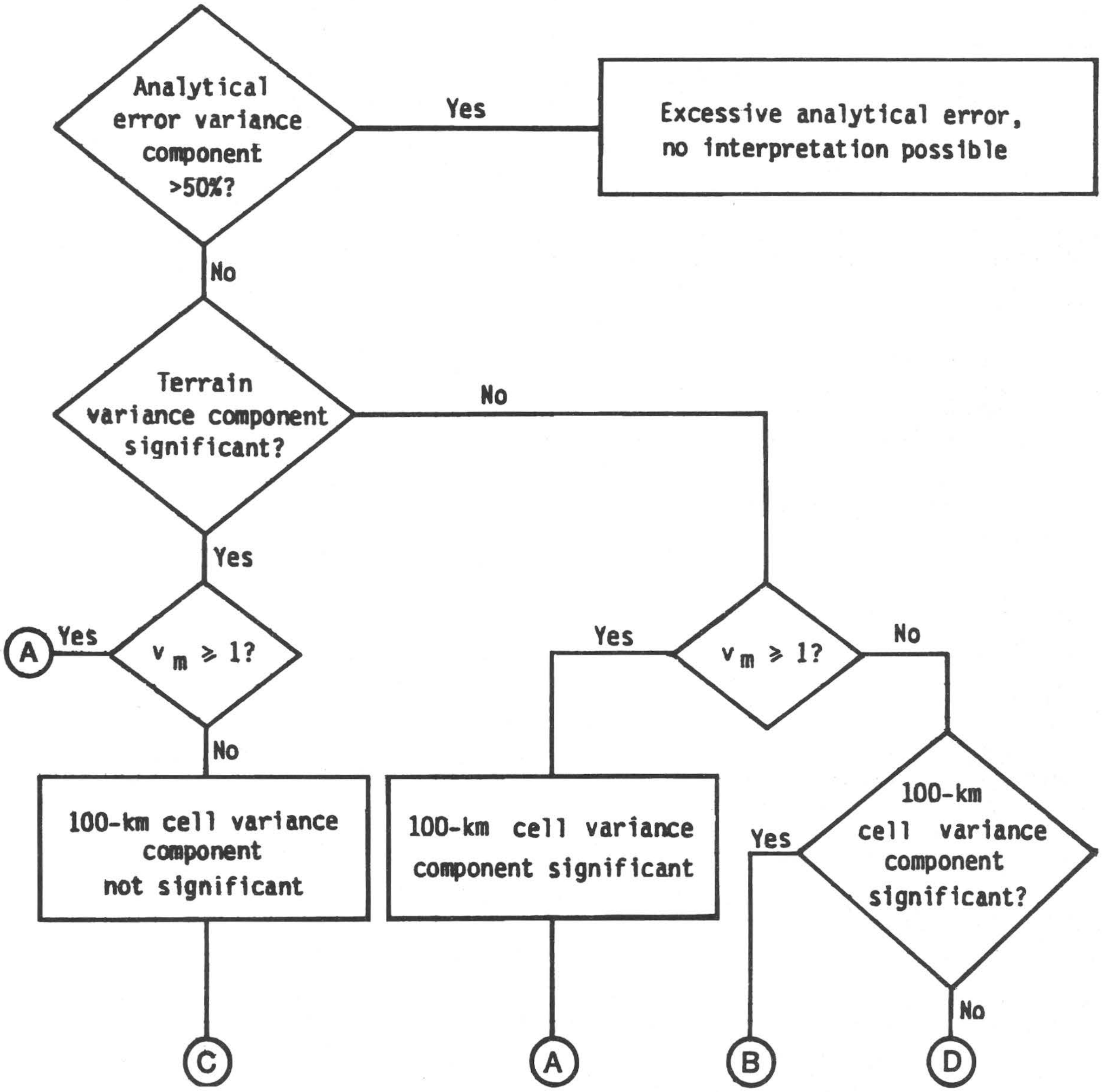
EXPERIMENTAL DESIGN

Possible experimental designs include, but are not limited to, simple random sampling, stratified random sampling, systematic grid sampling, and nested analysis of variance (ANOV). Nested ANOV has been the design of choice because it facilitates partitioning the total variance into components, each of which is associated with a source of variation.

The advantages of the nested ANOV are threefold. From a modest sample population, the variance components provide insight about (1) which sources of variation are important and which are not, (2) whether or not the initial sample population is sufficient to estimate stable means and baselines, and (3) whether the size of the sample population is statistically sufficient. If the sample population is shown to be adequate, then the data in hand provide an estimate of stable means and baselines. If the sample population is insufficient, then we know to which source of variation to direct a resampling.

THE NORTHERN GREAT PLAINS STUDY

The sources of variation measured in the northern Great Plains were glaciated terrain versus nonglaciated terrain, four levels of decreasing distance from 100 km to 1 km, and laboratory error (Severson and Tidball, 1979). An estimate of the magnitude of laboratory error with a threshold arbitrarily set at 50 percent of total variance helps to avoid interpreting error as a geographic effect. By partitioning the geographic part of the variance we determined the optimum method of data display (fig. 6.3) ranging in descending order of resolution from a stable map for elements having large regional variance to only a single value (grand mean) for the entire study area for elements having large local variance. The variance mean ratio



Ⓐ Reproducible map based on 100-km cell means with contours, see fig. 6.4*A*, uranium.

Ⓑ 100-km cell mean is single best estimate for each cell, no map, see fig. 6.4*B*, molybdenum.

Ⓒ Terrain mean is single best estimate for each terrain, no map, see table 6.1, mercury.

Ⓓ Grand mean is single best estimate for study area, no map, see table 6.2, boron.

Figure 6.3. Flowchart for choice of optimum method of data display (either map or computed mean) depending on the presence of significant variance components. Significance is at 0.05 probability level; v_m, variance mean ratio.

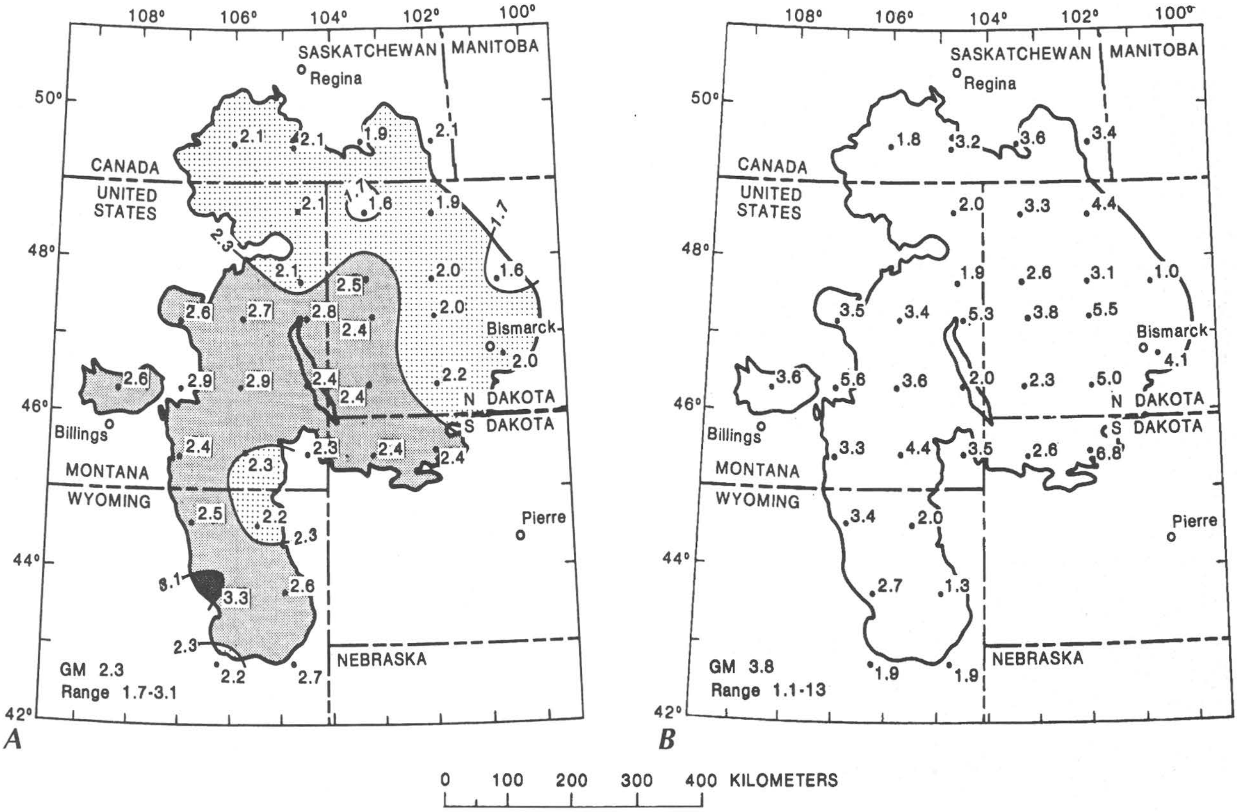


Figure 6.4. *A*, Uranium, 100-km cell means in parts per million (ppm), a mappable element having approximate contours. Patterned areas show frequency distribution in percent. Unpatterned area, less then 2.5 percent; light stipple, 2.5–5.0 percent; medium-gray, 50–97.5 percent; dark gray, greater than 97.5 percent. *B*, Molybdenum, 100-km cell means (ppm), no contours. From Severson and Tidball (1979).

(Severson and Tidball, 1979, p. A7), v_m, is the ratio of variance between different 100-km cells to that within individual cells. If the ratio is greater than one, a map of the cell means is considered to be stable and reproducible.

An example of a mappable element is shown in figure 6.4*A* for uranium. An example of a terrain mean is shown in table 6.1 for mercury. An example of an element that is best described by the means of individual 100-km cells is molybdenum (fig. 6.4*B*). The means are shown on a map to facilitate location, but no contour lines are shown. Both the mercury and molybdenum examples correspond to the case shown in figure 6.2*B*. An example of an element that is best described by a single grand mean is boron (table 6.2). This element corresponds to the case shown in figure 6.2*A*.

Table 6.1. Terrain mean and baseline for mercury (in parts per million) in soil samples of each terrain when the difference between terrains is significant but the difference within terrains is not significant

[Baseline, 95-percent expected range]

Terrain	Geometric mean	Baseline
Glaciated	26	13–51
Nonglaciated	21	9–44

Table 6.2. Grand mean and baseline for boron (in parts per million) in soil samples of entire study area when the difference between terrains is not significant

[Baseline, 95-percent expected range]

Element	Geometric mean	Baseline
Boron	41	18–96

OTHER DISTANCE-RELATED DESIGNS

Several soil studies have been designed by using distances having varying intervals. The intervals may be expressed by either irregular-shaped areas and cells of varying size or actual distance between sampling localities (barbell design; fig. 6.5). Some examples of studies that were designed by using areas of differing size similar to the northern Great Plains study include Connor, Keith, and Anderson (1976) in the Powder River Basin, Wyo.; Ringrose and others (1976) in the Piceance Creek Basin, Colo.;

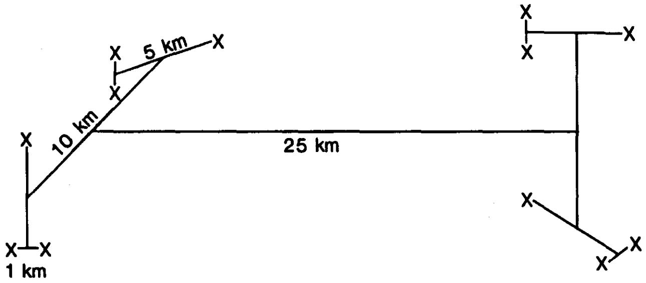


Figure 6.5. Diagrammatic representation of a barbell design. Sample localities shown as X's. From Severson (1979).

Tidball and Severson (1977) in the oil shale region of Colorado and Utah; Tidball (1978) in the Powder River Basin, Mont.; and Severson (1978a) in northwest New Mexico.

Examples of studies using the barbell design include Tidball and Ebens (1976) in the Powder River Basin, Mont.-Wyo.; Severson (1978b) in northwest New Mexico; and Severson (1979) in the Big Horn and Wind River Basins, Wyo.-Mont.

THE GENERAL SAMPLING PLAN

A general plan for geochemical sampling surveys of large regions was described by Connor and others (1972). The initial purpose is usually to distinguish the geochemical characteristics of some natural material that typically has mappable units. This general plan may be divided into at least four parts or stages, as follows:

Phase 1: Sampling to describe differences among categories.
  Stage 1a: Preliminary sampling designed to determine the extent to which the categories are indeed geochemically distinct and to provide the basis for planning stage 1b.
  Stage 1b: Final sampling to derive reliable estimates of differences among categories and the amounts of compositional variability within each category.
Phase 2: Sampling to describe patterns of variation within categories.
  Stage 2a: Preliminary sampling within each category to determine the sampling locality spacing that would be most efficient for describing the geochemical variation patterns within each category and the number of samples required from each locality.
  Stage 2b: Final sampling to describe the geochemical patterns within each category.

The first phase, which commonly is based on a limited number of samples, results in a geochemical map that has relatively poor resolution, but one that may be adequate if the variability is mostly on a regional scale. The second phase usually requires a larger number of samples and results in a map that has a higher resolution. This phase is used if the variability is mostly on a local scale.

The study in the northern Great Plains described above as well as other studies cited are all examples of stage 1a. Stage 1b was never completed. Although a sequential progression through the stages leads to maximum efficiency, circumstances sometimes do not allow time to perform stage 1a or 2a (for example, see Tidball and others, this volume).

When a stage 1b- or 2b-type map is required as soon as possible, how can this mapping be accomplished? One technique is to apply a simple random or perhaps a stratified random design to cover the area of interest. Another technique is to sample on a systematic grid. In each case, either the number of random samples or the grid interval is selected on the basis of some prior knowledge about the expected variation, if available, or selected on the basis of resources available. Once collected, there is no assurance that the number of samples will be adequate. However, by simultaneously collecting a few additional samples according to an ANOV design and the random or grid samples, we can determine that (1) the data are faulty and therefore interpretations are risky or incorrect, (2) the number of samples is about optimum and interpretations are safe, or (3) interpretations are safe, but the number of samples is excessive.

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7. Weathering Process Research—Pedology and Soil Geochemistry in Drainage Basins

By Milan J. Pavich

INTRODUCTION

As part of the proposed National Environmental Geochemistry Program, there is a need for studies of rock-weathering and soil-forming processes. Several U.S. Geological Survey (USGS) geologists and pedologists (scientists studying the genesis and classification of soils) have conducted research involving environmental geochemistry. Papers such as those published by Markewich and others (1986, 1987, 1988) and Pavich (1986) are the result of cooperative research with the U.S. Department of Agriculture's Soil Conservation Service (SCS) and university laboratories. Research into the geochemical processes operating during pedogenesis is still in an incipient stage. The National Environmental Geochemistry Program provides an opportunity for more research into pedogenic processes. Unlike geochemical surveys, process studies are best done as interdisciplinary studies in drainage basins.

The National Environmental Geochemistry Program can be divided into regional and topical studies; in many cases, these overlap. Soil geochemistry surveys are generally regional in scope, but specific topics or elements may be studied in areas as small as a single pedon, the unit of sampling comprising the A and B horizons and parent material, or in several pedons within a drainage basin.

We have developed the sampling and analytical techniques needed to obtain high-quality data from regolith. For this report, regolith is defined as that material through which ground water flows before discharge at the Earth's surface or material from which domestic water supplies are obtained through springs or by pumping. Regolith generally comprises soil, weathered rocks, sediments, and fractured crystalline rocks. Crystalline rocks of low permeability are excluded. The following sections provide an outline of how soils can be studied as part of the National Environmental Geochemistry Program.

DEFINITION OF SOIL

Soil can be defined in many ways. For the purpose of geochemical analysis, the definition given by Birkeland (1984, p. 3) is useful: "...a natural body consisting of layers or horizons of mineral and/or organic constituents of variable thicknesses, which differ from the parent material in their morphological, physical, chemical, and mineralogical properties...." This definition does not distinguish surface soils from buried soils. Study of the geochemical response of a specific soil to introduction of a specific element, or group of elements, usually involves the surface soil. In some cases, however, buried soils that have not been diagenetically altered since burial may provide useful geochemical information for comparison of past and present pedogenic environments (for example, climate, vegetation). Surface soils are mapped and classified in the United States according to taxonomic principles developed by the SCS (Soil Survey Staff, 1975).

SOIL TAXONOMY

The SCS Soil Taxonomy (Soil Survey Staff, 1975) classifies soils of the United States into 10 orders. These taxonomic divisions reflect a strong influence of climate, as seen on fig. 7.1, and also of parent material and physiographic setting. At present, we do not have sufficient knowledge to discuss the detailed evolution or genesis of individual suborders or soil series within these broader orders.

The dominant soil orders in populated areas are mollisols, alfisols, and ultisols. Mollisols are distinguished by dark, organic-rich A horizons (mollic epipedon) and base saturation (a measure of exchangeable nutrients) greater than 50 percent throughout. Alfisols have lighter

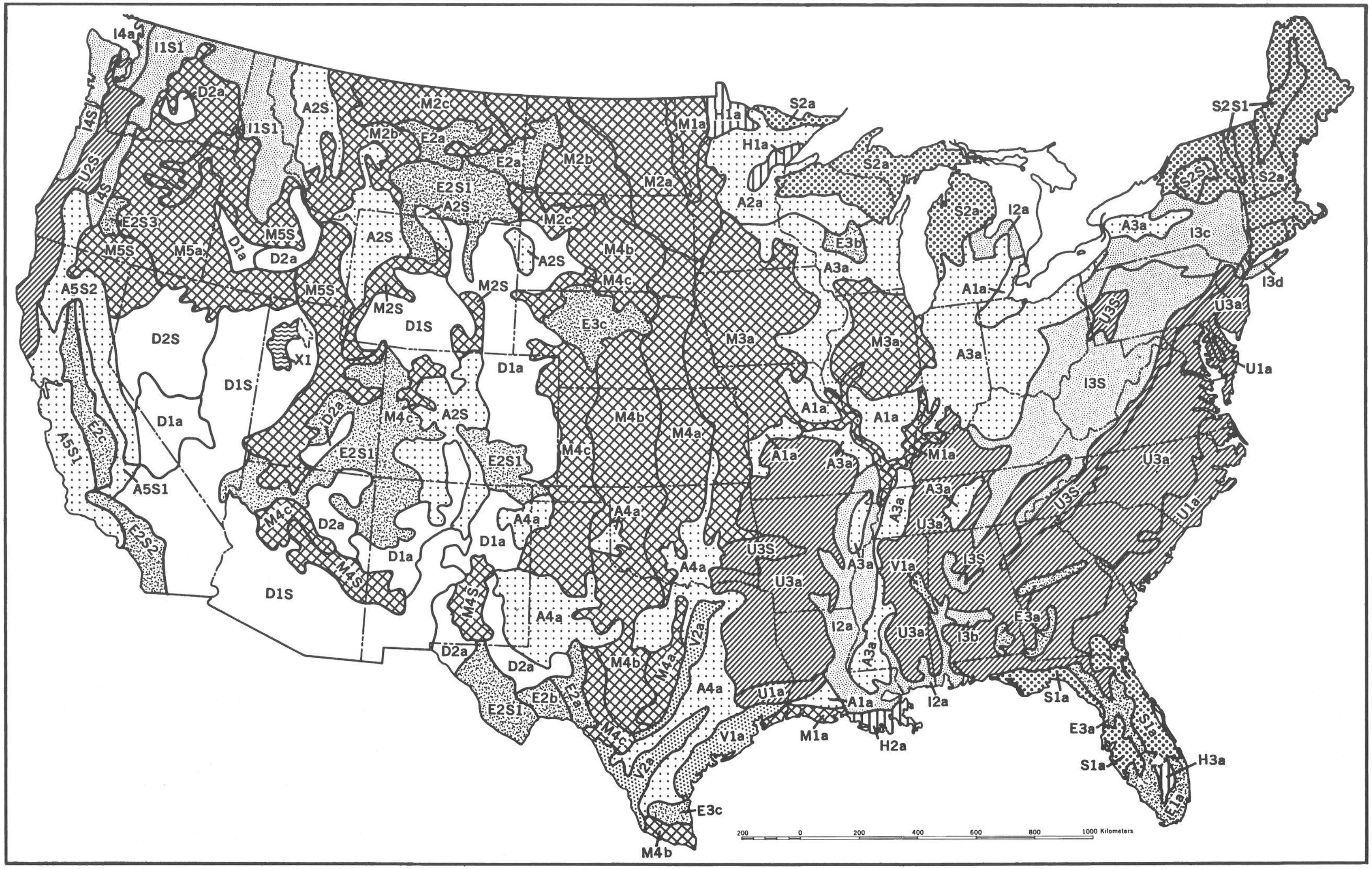

Figure 7.1. Generalized soil map of the conterminous United States. Major soil groups represented by initial capital letters on map are as follows: A, alfisols; D, aridisols; E, entisols; H, histosols; I, inceptisols; M, mollisols; S, spodosols; U, ultisols; V, vertisols. Modified from Soil Survey Staff (1975), where further information regarding soil taxa may be found.

colored A horizons (ochric epipedon), an argillic (clay-rich)horizon, and base saturation exceeding 35 percent in the argillic horizon. Ultisols are characterized by having base saturation less than 35 percent in the argillic horizon. In all of these soil orders, A and B horizons can be distinguished.

HYDROCHEMICAL PROCESSES IN MAJOR SOIL ORDERS

The full range of geochemical processes operating in these major soil orders is extremely complex. Identified capacities of soils that influence movement of chemical elements include:

(1) Cation-exchange capacity (CEC) of fine particulates (for example, clays, iron oxyhydroxides) and organic materials that are found in many soils. CEC is usually measured in terms of milliequivalents of cation per 100 grams of solid (meq/100 g). Exchange capacities range from 2–4 meq/100 g for sesquioxides to 200 meq/100 g for humus (Tan, 1982). Base saturation is the percentage of CEC occupied by exchangeable bases (for example, Ca^{+2}, Mg^{+2}, K^{+}, Na^{+}).

(2) The water-holding and infiltration capacities of soils runoff in response to rainfall. Runoff is an important characteristic of drainage basins that partially determines how dissolved and suspended materials, including pollutants, are moved from upland soils into surface-water discharge.

Interaction between solids (for example, clay minerals, precipitated humic organic matter, other minerals) and elements entering the soil generally involves solid-solution chemical reactions, mainly at particulate surfaces. Surface reactions are varied and complex and are a topic of active research. Soil process studies should include surface chemistry.

SAMPLING AND ANALYTICAL TECHNIQUES

The geochemical assessment of any selected area requires a well-designed sampling scheme. For soil-survey work, the Soil Survey Staff (1984) has developed a scheme using transects, paired pedons, and satellite pedons. They stress that site selection should be based on choosing a pedon representative of the mapping unit and of the landscape being studied. Site selection is not random in their scheme. The same sampling schemes may not be appropriate to soil-genesis studies and geochemical surveys.

Nested analysis of variance (Miesch, 1976) was used in the geochemical surveys of McNeal and others (1985) and Severson and Tidball (1979). They sampled mollisols in the northern Great Plains, an area of potential strip mining for coal. These studies demonstrate that efficient sampling schemes are possible for characterization of soil chemistry over a large area. Studies of soil genesis may require sampling schemes related more to the variability of parent material and landscape.

CONTROL SECTIONS

The drainage basin is the natural study site for biogeochemical processes, particularly mass and energy flows. The size of the basin considered is dependent upon the research goals. For geochemical research, relatively small basins on homogeneous parent materials are best. Hydrologic and geochemical mass-balance techniques are applicable to a wide range in size of drainage basins.

Soils are mapped as geomorphic (morphostratigraphic) units in drainage basins. They are the locus of much mass and energy transfer among the atmosphere, lithosphere, biosphere, and hydrosphere. On the 10- to 100-year time scale of contaminant accumulation, they can be viewed as complex ion-exchangers or adsorbers of metals.

Soils evolve over geologic time toward steady states influenced by climate, vegetation, and parent rock (Birkeland, 1984). The energetics of biological, chemical, and mechanical processes operating in the soil are balanced over a long time period. Research should include study of long-term pedogenic processes, as well as topical studies of contaminant loading.

To facilitate the resampling of representative pedons, control sections should be established in drainage basins under investigation by the USGS. Undisturbed preserves are needed to ensure access to these control sections. Ideally, these preserve areas will be at least 1 km^2, be on uniform rock types or parent material, and be within drainage basins that are part of the USGS National Water Quality Assessment Program (NAWQAP).

RECOMMENDATIONS FOR PROGRAM INITIATION

1. Select sampling areas from basins being studied in NAWQAP.

2. Identify major soil types in each study basin or area.

3. Devise a sampling and analysis scheme that will utilize USGS expertise and allow characterization of large areas. For example, pick those soils that are typical of the study area or those that are considered most sensitive to chemical alteration by pollutants (for instance, soils having low buffering capacity for acidity in areas of acid-rain research).

4. Establish type sections that can be resampled at intervals. Unlike streams or ground waters, which can be sampled nondestructively, soil sampling is in itself an

alteration of the natural state of the soil. Care must be taken in establishing sites and methods that allow for periodic assessment of change.

5. Use USGS and SCS expertise in the analysis of pedons characteristic of soil series (the basic soil mapping unit) and in the interpretation of data. A large data base exists within SCS files. This should be used where possible.

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8. The Mode of Occurrence of Extractable Elements in Soils from the Northern Great Plains

By James M. McNeal

As concerns increase about possible trace-element contamination of the environment, it becomes even more important to study the manner in which elements occur in the natural environment (rocks, soils, sediments, water). These studies are particularly useful in determining the release, transport, and sorption of elements in the environment. Numerous studies have examined the variation in the total-element content of environmental samples, but most have not examined the mode of occurrence (the chemical form of an element and the mineral phase or phases with which the various forms may be associated) of elements in the samples. Understanding the mode of occurrence of elements in these materials is important because some modes of occurrence of an element may not pose a hazard for living organisms, whereas some others may be particularly deleterious. In addition, the potential occurrence of some environmental problems may be predicted on the basis of the mode of occurrence of an element, coupled with knowledge of the local geochemical regime.

In general, two methods are used to examine the mode of occurrence of an element. The first method is to determine a number of chemical, physical, and mineralogical variables on several related samples. Then, a variety of statistical and mathematical tools are used to determine the relations between the elements and the chemical, physical, and mineralogical variables. These associations are then interpreted scientifically according to geochemical principles. The modes of occurrence of an element are interpreted accordingly.

The second method is to treat a sample with a carefully predetermined series of chemical extractants. Each extractant acts on the residue from the previous treatment. The modes of occurrence of an element are then interpreted from the concentration of the element in the extractant solution and the physical-chemical portion of the sample attacked by the extractant. Chao (1984) provided a comprehensive review of partial dissolution techniques.

This paper reviews an example (McNeal and others, 1985) of how the modes of occurrence of elements in soils were determined and shows which modes of occurrence are attacked by each of these commonly used soil extractants. Studies of this type are necessary for gaining insight into the uptake of elements by plants and into the transport of elements in the environment. Details of this study were reported by McNeal and others (1985). A parallel study (Gough and others, 1979) was conducted to determine the relation between element uptake by native plants and the concentration of elements in soils by using the same chemical extractants.

The soil samples were collected from 21 locations from the northern Great Plains (generally eastern Montana, western North Dakota, northwestern South Dakota, and northeastern Wyoming). The locations represent localities of extreme differences (as determined by Q-mode factor analysis) in soil composition based on the total-element concentration of soils studied by Severson and Tidball (1979).

A large number of variables were determined in this study—90 variables for the A horizon and 79 for the C horizon. Among the variables determined were total-element concentrations for Ca, Cu, Fe, K, Mg, Mn, Na, Ni, and Zn. The following elements were generally determined on the solutions from the six extractants for both soil horizons: Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, and Zn. The extractants included are, from the mildest to the strongest, $Mg(NO_3)_2$, diethylenetriaminepentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA), hydroquinone, ammonium oxalate, and hydrochloric acid (HCl). The HCl extraction was not done on the C-horizon soils. These extractants were selected because they represent a broad range of different kinds of chemical attack and are commonly used by soils scientists to investigate the availability of elements in soils to plants. The mineralogy of each sample was estimated by using a semiquantitative X-ray diffraction technique. Several other commonly determined chemical and physical soil properties also were determined.

R-mode factor analysis was used in this study to express the associations among the large number of variables in terms of a smaller number of master variables. The associations among the variables are related to the factors on the basis of their loadings on each factor. Factor loadings

Table 8.1. The relative order of importance of factors for all extractable elements (from McNeal and others, 1985)

[Factors are derived by R-mode factor analysis and varimax rotation in A and C horizons of soils of the northern Great Plains. CEC, cation-exchange capacity; (−), loadings are negative]

Extractable element	Soil horizon	
	A	C
Cadmium	Organic = Iron and manganese oxides	Iron and manganese oxides > Soluble sodium
Calcite	Clay > Organic = Soluble sodium	CEC
Cobalt	Iron and manganese oxides > Organic	Iron and manganese oxides = Clay = CEC
Copper	Iron and manganese oxides > Clay = Organic	Iron and manganese oxides = Clay = CEC = Iron and manganese
Iron	Clay > Iron and manganese oxides	Iron and manganese oxides > Clay
Lead	Organic > Clay > Soluble sodium	CEC > Iron and manganese = Clay
Magnesium	Clay > Soluble sodium = Organic	Clay > Iron and manganese oxides (−)
Manganese	Iron and manganese oxides > Soluble sodium >Clay	Iron and manganese oxides > CEC (−)
Nickel	Iron and manganese oxides	Iron and manganese oxides
Potassium	Organic	Clay
Sodium	Soluble sodium > Clay	Soluble sodium
Zinc	Organic > Iron and manganese oxides = Clay	Iron and manganese = Iron and manganese oxides (−) = CEC

are analogous to correlation coefficients. The modes of occurrence of the extractable elements in the soils were interpreted in geochemical terms on the basis of the magnitude of their loadings on each factor.

Four factors (organic, clay, iron and manganese oxide, and soluble sodium) were found for the A-horizon soils, and seven factors (carbonate, clay, cation-exchange capacity (CEC), soluble sodium, organic, total iron and manganese, and plagioclase) were found for the C-horizon soils. About 75 percent of the total variance for each horizon was explained by the factor models. The relative importance of each factor for each extractable element is shown in table 8.1 by soil horizon.

Each of the extractable major elements (calcium, potassium, magnesium, and sodium) generally occurs with one factor, regardless of the extractant used. In the A horizon, extractable calcium and magnesium are related to the clay factor, extractable potassium to the organic factor, and extractable sodium to the soluble-sodium factor. In the C horizon, extractable calcium is related to the CEC factor, extractable potassium and magnesium to the clay factor, and extractable sodium to the soluble-sodium factor. These results suggest that extractable major elements are water soluble and are associated with the constituents that are responsible for that factor.

The extractable trace elements (Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn) for both the A and C horizons are most closely associated with iron and manganese oxides, based on high loadings with the iron- and manganese-oxide factors. In the A horizon, the extractable trace elements also have a weak association with the organic factor. The CEC and clay factors are also of some importance for trace elements extracted from the C-horizon soils. These results suggest that iron and manganese oxides are the most important residence of these extractable trace elements in these soils, underscoring the importance of iron and manganese oxides in controlling the release, transport, and sorption of these extractable metals in the environment.

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9. Uranium-Series Disequilibrium in Quaternary Soils—Significance for ^{222}Rn Hazard Assessment

By Daniel R. Muhs, Charles A. Bush, *and* John N. Rosholt

INTRODUCTION

Radon and its daughter products have been identified as major sources of environmental radiation. Estimates of the amount of exposure to human beings indicate that this radiation may be a leading cause of lung cancer (Evans and others, 1981). An important part of studies that assess the potential radon hazard is accurate measurement of natural radioactivity in the surficial geologic environment or soil zone. Sources of surficial geologic radioactivity on a regional scale can be measured by laboratory estimates of quantities of uranium, thorium, and potassium in typical mapped geologic units or by airborne gamma spectrometric surveys. In both of these methods, assumptions are made about the distribution of uranium and its decay products, including ^{222}Rn (fig. 9.1), in soils and surficial geologic materials. In this paper, we show that the distribution of uranium and its decay products in soils can be complex and difficult to predict.

Uranium has considerable mobility in oxidizing near-surface environments, where it can occur in the relatively soluble (U^{+6}) state. A portion of the uranium released by weathering of some soil constituents may be adsorbed by other constituents such as clays, organic matter, manganese oxides, and iron oxides (Rosholt and others, 1966; Ames, McGarrah, Walker, and Salter, 1982, 1983; Ames, McGarrah, and Walker, 1983a). The degree to which uranium is sorbed depends upon solution chemistry, pH, Eh, the type and abundance of competing cations and complexing agents, surface properties (crystallinity, cation-exchange capacity), and the rock-to-water ratio (Langmuir, 1978; Giblin and others, 1981; Tsunashima and others, 1981). In bicarbonate-rich waters, uranium can migrate as anionic carbonate and hydroxide complexes (Langmuir, 1978).

Thorium, in contrast to uranium, is characterized by extreme insolubility in most low-temperature surficial environments (Langmuir and Herman, 1980), and ^{230}Th generated by decay of ^{234}U is predicted to be relatively immobile. However, if thorium is introduced into an organic-rich environment, some mobility as soluble organic-thorium complexes may be possible (Hansen and Huntington, 1969; Langmuir and Herman, 1980). ^{230}Th that is adsorbed by clays may migrate via physical transport of the clays (eluviation and illuviation).

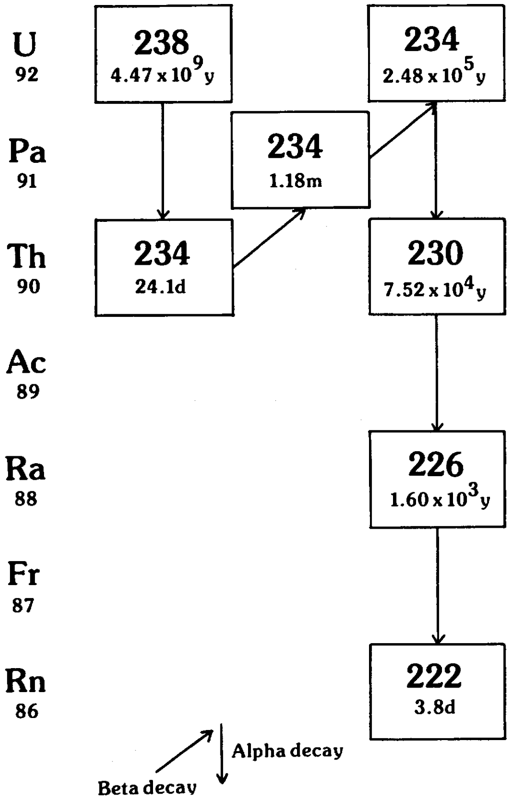

Figure 9.1. The upper part of the ^{238}U-series decay chain, showing nuclides and their half-lives discussed in this paper.

The mobility of ^{226}Ra is of particular interest because it is the immediate parent of ^{222}Rn. There are studies of the distribution and mobility of radium in soils, but apparently radium generally behaves in a manner similar to that of other alkaline earth elements, such as calcium, magnesium, strontium, and barium. Studies by Nathwani and Phillips (1979) indicate that ^{226}Ra is adsorbed by clays and organic matter; organic matter may sorb more radium than clays in the same horizon by as much as a factor of 10. Ames and others (1983a,b) conducted experimental studies that showed that radium can be adsorbed onto clinoptilolite, illite, nontronite, phlogopite, and biotite; sorption efficiency was related to the cation exchange capacity of the minerals. These same workers found that, under identical conditions, radium sorption is greater than uranium sorption. Ames, McGarrah, Walker, and Salter (1983) found that radium is also sorbed by iron oxyhydroxides and that sorption is greatest when radium concentrations are high and concentrations of competing alkaline earth elements are low.

Over the past few years, we have studied the mobility and distribution of ^{238}U, ^{234}U, ^{230}Th, and ^{226}Ra in near-surface environments by measuring the relative alpha activities of alpha-particle-emitting isotopes in Quaternary soils. Determinations of the alpha activities of ^{238}U, ^{234}U, ^{232}Th, and ^{230}Th were made by isotope dilution and alpha spectrometric methods (Rosholt, 1984, 1985). The activity of ^{226}Ra and an independent measurement of ^{232}Th concentration were made by gamma spectrometry (Bunker and Bush, 1966).

Our preliminary conclusions are based on analyses of 124 soil horizons from 17 soil profiles. The soils are from Quaternary deposits in California, Nevada, New Mexico, Colorado, and the island of Barbados, West Indies. Parent materials for the soils are mostly alluvium but also include eolian sands and silts, glacial till, and mixtures of volcanic ash and airborne dust. The ages of the deposits range from middle Pleistocene to Holocene, and climates range from arid to humid tropical.

RESULTS AND DISCUSSION

Results of radiometric analyses of the 17 soil profiles indicate that roughly half of the profiles have ^{234}U/^{238}U activity ratios of 1.00 or, in other words, show radioactive equilibrium. Radioactive equilibrium is defined as a condition where, on the average, there is decay of one parent atom for each decay of a daughter atom. In contrast, disequilibrium is a condition where the activity of a daughter isotope is greater or less than that of its parent. The other half of the profiles show ^{234}U/^{238}U ratios greater than unity, indicating radioactive disequilibrium, with values ranging as high as 1.30 but more commonly in the range of 1.05–1.20. The frequent excess of ^{234}U over its parent ^{238}U in surface waters is well documented and results from the preferential leaching of decay-generated ^{234}U atoms from mineral surfaces via alpha-recoil mechanisms (see discussions in Rosholt, 1983, 1985). Thus, the ^{234}U/^{238}U ratio that measures greater than 1.0 in modern soils may simply indicate adsorptive uptake of some dissolved uranium from coexisting waters passing through the soils. Alternatively, if quantities of the first three daughters of ^{238}U (^{234}Th, ^{234}Pa, and ^{234}U) are produced by radioactive decay during the passage of uranium-bearing water through the soil, they may be preferentially emplaced via a mechanism of recoil from the liquid phase onto solid surfaces. In a chronosequence of soils from New Mexico, we found that the ^{234}U/^{238}U alpha activity ratios tend to increase over time; that is, soils that are 22 ka and 130 ka had alpha activity ratios near equilibrium values (0.98–1.03 and 0.96–1.06, respectively), whereas soils that are ~290 ka and ~420 ka had activity ratios significantly higher than equilibrium (0.98–1.17 and 1.12–1.30, respectively). ^{234}U/^{238}U activity ratios as high as 14.0 have been reported for Quaternary sediments elsewhere (Szabo, 1982). Study of Tertiary zeolites in Utah indicates, however, that, over much longer periods of geologic time, preferential displacement of ^{234}U by selective leaching may predominate over recoil emplacement or adsorption of ^{234}U (Rosholt, 1980).

Disequilibrium of ^{230}Th and ^{226}Ra with regard to their respective parents is also observed in the soils we studied. As a first approximation, we have classified the observed disequilibrium into four general categories. The first category, seen in two soils from New Mexico and Colorado, is characterized by ^{230}Th/^{234}U ratios greater than 1.0 in most or all of the profile but ^{226}Ra/^{230}Th essentially in equilibrium (fig. 9.2). This type of disequilibrium can be

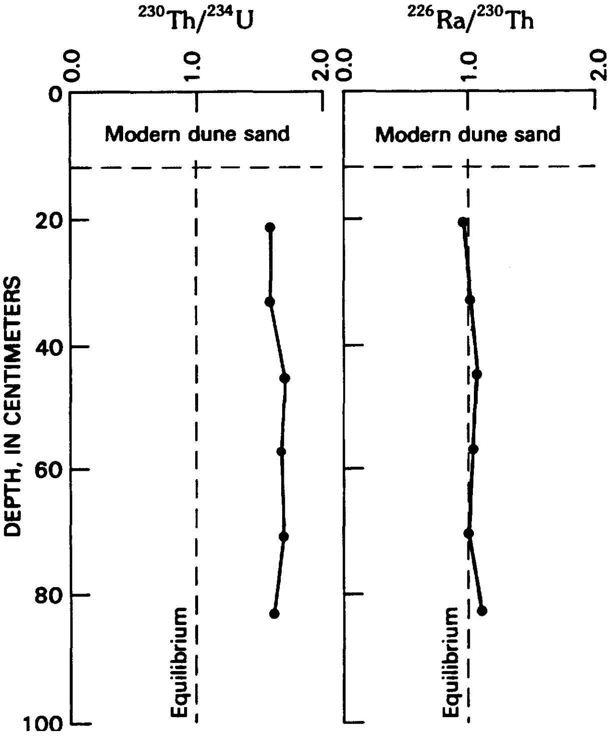

Figure 9.2. Category 1 disequilibrium in the Berino soil (unit CQS) from Eddy County, N. Mex. The soil was developed in eolian sediments and has a uranium-trend age estimate of 360±160 ka (J.N. Rosholt, unpub. data). Analytical errors are ±1.6 percent (1 σ) for ^{230}Th/^{234}U and ±8 percent (1 σ) for ^{226}Ra/^{230}Th.

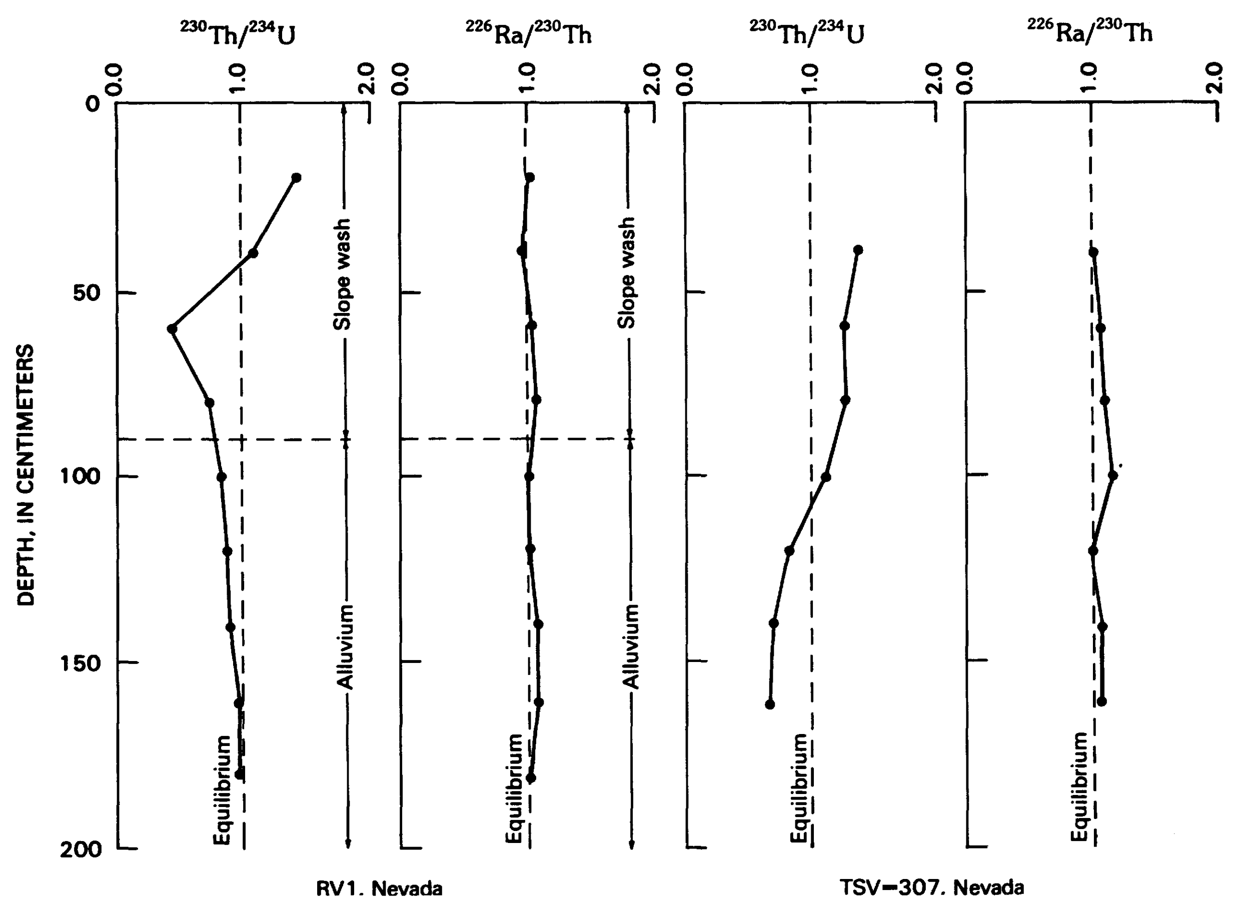

Figure 9.3. Category 2 disequilibrium in two soil profiles from the Nevada Test Site. RV1 consists of two superposed soil profiles developed in slope wash over alluvium; uranium-trend dates are 31±10 ka and 310±40 ka, respectively (Rosholt and others, 1985). Unit TSV–307 is developed in alluvium and has a uranium-trend date of 38±10 ka. Analytical errors are the same as those given in figure 9.2.

explained by either or both of two processes: leaching of ^{234}U after decay generation of some ^{230}Th or gain of particles with unsupported (that is, ^{234}U-depleted) ^{230}Th. The added particles could be eolian clays that are leached of uranium but that retain the less soluble ^{230}Th daughter.

A second category of disequilibrium is a variation of the first, where there is again a ^{230}Th/^{234}U excess in surface horizons, but a ^{230}Th/^{234}U deficiency at lower depths. Soils from New Mexico and Nevada illustrate this phenomenon, and we suggest that this phenomenon represents leaching of uranium, particularly ^{234}U, from upper parts of the profiles and its accumulation at lower depths (fig. 9.3).

Greater complexity is illustrated by the third category of disequilibrium in which both ^{230}Th/^{234}U excesses and ^{226}Ra/^{230}Th excesses are found in most horizons. Soils from Nevada and New Mexico provide typical examples of this category, and soils from Barbados illustrate an extreme example of ^{230}Th/^{234}U excess (fig. 9.4). In the case of Barbados, the dominant process of ^{230}Th/^{234}U excess is almost certainly uranium leaching via intense tropical weathering, because soil parent materials (volcanic ash from St. Vincent and airborne dust from Africa) have ^{230}Th/^{234}U ratios that are 1.0 (equilibrium) or are actually less than unity (Rydell and Prospero, 1972; Muhs and others, unpub. data). In Nevada and New Mexico, intense chemical weathering is less likely, and we suggest that the ^{230}Th excesses are most likely due to eolian input of airborne clays and silts having unsupported ^{230}Th. Interestingly, the excess of ^{226}Ra over its parent ^{230}Th suggests that, in New Mexico and Nevada, two eolian sources may be involved, one having unsupported ^{230}Th and one having unsupported ^{226}Ra. On Barbados, we lack ^{226}Ra data for the soil parent materials, but on the basis of ^{222}Rn measurements reported by Carlson and Prospero (1969), we suspect that unsupported ^{226}Ra is present in the airborne dust from Africa. For all soils of the third category, at least some processes have taken place during the Holocene, because ^{226}Ra is not yet in radioactive equilibrium with ^{230}Th.

The fourth category of disequilibrium is a simplified version of the third category. ^{226}Ra/^{230}Th values are again greater than unity, but ^{230}Th/^{234}U ratios are at equilibrium values or are even less than unity. Certain soils from New

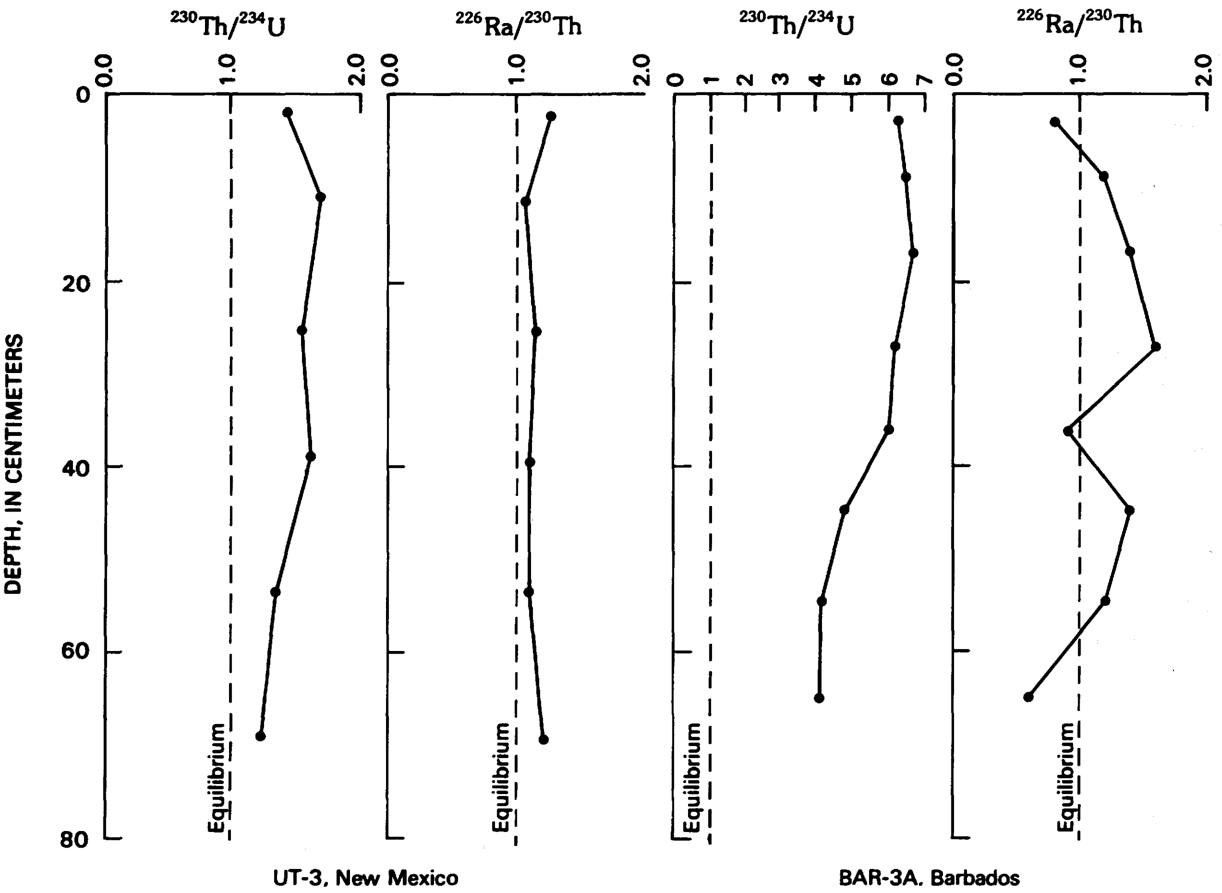

Figure 9.4. Category 3 disequilibrium in soil profiles developed in Izaac's Ranch alluvium (UT–3), southern New Mexico (Gile and Grossman, 1979), and on the Rendezvous Hill coral terrace (BAR–3A), Barbados. Ages are 22±15 ka (uranium-trend) and about 125 ka (uranium-series), respectively. Analytical errors are similar to those given in figure 9.2.

Mexico and the San Joaquin Valley of California fall into this category. We suspect that the observed $^{226}Ra/^{230}Th$ excesses may be explained by Holocene additions of unsupported ^{226}Ra via airborne silts and clays, but the mechanism by which the ^{226}Ra excess is produced has not been identified. Radium mobility in arid environments resulting in disequilibrium on eolian particles has been suggested by other investigators (Hirose and Sugimura, 1984). Alternatively, ^{226}Ra may enter the soils in waters that pass through the soils subsequent to parent material deposition and soil formation.

CONCLUSIONS

The observations we have summarized here suggest that radioactive disequilibrium of the uranium series is a common occurrence in soils of Quaternary age. Excesses of ^{234}U over its parent ^{238}U are observed in about half of the soils that we examined and are probably due to adsorption of dissolved uranium and the daughter-emplacement process as dissolved uranium and daughters pass through the soil profiles. Other indications of disequilibrium such as alpha activity of $^{230}Th/^{234}U$ greater than 1.0 may be explained by either eolian additions of unsupported ^{230}Th or, in the case of tropical environments, loss of uranium through weathering processes. Excesses of ^{226}Ra over its parent ^{230}Th may be due to additions of airborne dust that have unsupported ^{226}Ra. Other studies have documented that certain of our study areas, such as the Rio Grande Valley of New Mexico, the San Joaquin Valley of California, and Barbados, are localities that receive significant quantities of airborne dust (Gile and Grossman, 1979; Prospero, 1981; Wilshire and others, 1981; Muhs and others, 1987). Similarity of uranium-series disequilibrium in the Nevada soils indicates that eolian additions may be important in that locality as well.

Our observations have significance for ^{222}Rn hazard-assessment studies. Some preliminary assessments have been made by using airborne gamma spectrometric data and geologic maps. In situations where soils are derived largely from the underlying consolidated rocks, there is a good match between the derived radioactivity maps and the uranium, thorium, and potassium contents of the bedrock units (Pitkin, 1968; Schwarzer and others, 1972; Schwarzer and Adams, 1973). However, because airborne surveys measure only the radioactivity of the upper 50 cm or less of the soils (Duval and others, 1971), deeper horizons that have high activities of ^{230}Th and ^{226}Ra (and thus sources for ^{222}Rn), such as we have observed, are not measured. In areas where ^{230}Th and ^{226}Ra are found on eolian particles, the radioactivity of the upper soil horizons may be unrelated to the uranium content of the underlying rocks. Thus, our observations of uranium-series disequilibrium in soils suggest that both geologic maps and airborne surveys provide only general indicators of the radioactivity of soils.

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10. Biogeochemical Baselines and the Importance of Species, Plant Parts, and Season—The U.S. Geological Survey's Studies of Big Sagebrush in the West

By James A. Erdman

Unlike nonliving sample media, such as rocks or soils, the effects of species (or even subspecies and cultivars), plant parts, and season can seriously flaw attempts to develop element-compositional baselines for plants. Such effects must be considered in designing baseline studies that include vegetation. The U.S. Geological Survey's (USGS) experience with big sagebrush (*Artemisia tridentata* Nutt.) underscores some of the success, as well as problems, encountered in the field of environmental geochemistry.

The sole basis for selecting sagebrush is simple—the sagebrush-grass vegetation makes up one of the largest range ecosystems in the Western United States. It extends over much of Utah, Nevada, southern Idaho, eastern Oregon, western Montana, and Colorado, as well as smaller areas in Washington, California, Arizona, and New Mexico.

REGIONAL BASELINE STUDIES

The first efforts by the USGS to establish regional-scale baselines for native plants and cultivated crops were conducted as part of a cooperative study with the Environmental Health Surveillance Project at the University of Missouri, Columbia (Erdman and others, 1976a,b). Following that work, efforts were focused on possible geochemical changes that might result from the reclamation of surface coal mines in the West. To assess such changes, baselines had to be developed for regions that might be affected. Initial attempts to establish baselines for big sagebrush began in the northern Great Plains lignite province, in particular the Powder River Basin (Tidball and others, 1974; Connor and others, 1976), and used nested barbell or gridded sampling designs.

The most extensive baseline study of big sagebrush involved the collection and analysis of samples from 190 sites in 8 physiographic provinces of the West (see figure 3.3 in Shacklette, this volume). In this study, Gough and Erdman (1983) used an eight-level analysis-of-variance design to "take into account the predominant scales of geochemical variability inherent in nature" (Connor and others, 1976, p. 49). Such an account is a mandatory requirement of any attempt to establish geochemical baselines.

The general conclusions of the three baseline studies of big sagebrush mentioned above are that baselines are best expressed as ranges of element concentrations, such as the central 95-percent range, a definition of baseline first proposed by Tidball and Ebens (1976). Results of the analysis-of-variance sampling designs clearly showed the importance of small-scale (local) element variation in sagebrush. Estimates of this variation indicated that samples of sagebrush collected at opposite ends of the regions or physiographic provinces generally differed little more than samples taken only several miles apart. Mapping the distribution of elements would have been useless for the most part; considerably more effort would have been needed, including perhaps resampling the region, to ensure stable geochemical maps.

One result of the study by Gough and Erdman (1983) was the evidence of possible uranium mineralization in southwestern Idaho (Erdman and Harrach, 1981). In response to that paper, Diebold and McGrath (1985) conducted a detailed study of the anomaly and, through hydroponic experiments, investigated the effect of groundwater chemistry on the uptake of uranium by big sagebrush.

TOPICAL STUDIES

Big sagebrush is a highly polymorphic species. Three subspecies (ssp. *tridentata*, *wyomingensis*, and *vaseyana*) are generally recognized. Because identification of these subspecies in the field is difficult, even for brushland taxonomists, Gough and Erdman (1983) considered big sagebrush as a single taxonomic entity. Results of a uniform garden-plot study conducted in 1978 of the three recognized subspecies (J.A. Erdman, unpub. data) indicated that significant differences in concentrations of some elements in leaf samples do exist. Yet they seem to be minor compared with those differences observed among the provinces. Nevertheless, such genetic effects need to be assessed in any baseline study.

Seasonal effects may be equally important. Gough and Erdman (1980) sampled a stand of Wyoming big sagebrush over a period of 1 year and found that seasonal changes in the concentrations of the major elements reflect phenological events that alter the proportion of leaf-to-stem tissue in the samples. In general, the element composition of younger tissue fluctuated more, had higher concentrations, and showed greater differences among seasons than did the older material. These results underscore the importance not only of season, but also of plant part on element concentrations. Erdman and Olson (1985) reported that, in the Soviet Union, where sagebrush has seen considerable use in mineral prospecting, sampling of *Artemisia* (wormwood) is conducted in the spring when the gold concentrations in ash are about 10 times the levels observed in the fall (80–85 parts per million (ppm) in May and only 4–8 ppm in October).

In summary, baselines for element concentrations in plants are attainable, but sampling should be completed in a relatively short period of a single season and certainly not extended from one year to the next. Unlike efforts to achieve such data for rocks and soils, considerations of the effects of genetics, parts, and season are mandatory for plants.

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11. Vegetation Studies in the Northern Great Plains

By Larry P. Gough

INTRODUCTION

Between 1974 and 1978, the U.S. Geological Survey (USGS) was actively involved in the environmental geochemical and biogeochemical characterization of the northern Great Plains as it related to present and projected surface-coal mining activities. Regulations governing the reclamation of mined land require that the land be returned to its former use, which, in the northern Great Plains, is mainly pasture and small-grain production. Therefore, an assessment of the impact of surface mining in this region must include a consideration of the possible effects on the growth and chemical characteristics of both agricultural species, utilized by man, and native plant species, utilized by grazing animals. As part of the USGS Energy Lands Program, biogeochemical studies in this region focused on three broad topics: (1) chemical-element characterization of small grains; (2) chemical-element characterization of native species and of their relation to the availability of major and minor nutrient elements and environmentally important metals in soils at geochemically diverse sites; and (3) comparison of the chemistry of native and introduced pasture species growing in both rehabilitated mine sites and adjacent undisturbed sites, as well as the relation of these species to soil chemistry.

NATIVE-SITE METAL AVAILABILITY AND UPTAKE BY PLANTS

Agricultural Species Studies

A hierarchical-nested analysis of variance (ANOV) design was used in the sampling of hard-red spring and hard-red winter wheat grains on lands undisturbed by surface mining throughout the northern Great Plains, including the southern edge of Saskatchewan, Canada. This design enabled the partitioning of the variability in the elemental concentration of wheat among various geographic scales (Erdman and Gough, 1979). The regional variability information was used as an aid in the estimation of biogeochemical baseline values, as defined by Tidball and Ebens (1976). These baseline data then were used to compare the chemistry of wheat grown on topsoiled spoil material among several surface-coal mines.

Native Species Studies

Twenty-one study locations in the northern Great Plains were identified on the basis of their geochemical variability (fig. 11.1) (Severson and others, 1977; Gough and others, 1979). Material sampled at each location included western wheatgrass, silver sagebrush, total aboveground plant biomass, and A and C soil horizons. Both total and extractable element levels in soil were examined.

Bioavailability measures.—Total element levels in plants can be considered as representing the bioavailable fraction of the soil. In addition, biomass samples measure the biogeochemical load in the vegetation. Biomass sampling is a means of studying the bioavailable metal levels of a region and not just of a species. As examples, biomass ranged from 200 kg/ha at a heavily grazed Montana site to 1,800 kg/ha at a Wyoming site and resulted in load estimates of copper, 0.3–2.2; iron, 12–410; and zinc, 7–56 g/ha.

Native-soil and plant-element relations.—Metal concentrations in A and C soil horizons showed large geochemical variability between sites in both the total digestions and in the extractions. Samples of herbage, however, showed very little variability. A stepwise multiple regression analysis was used to study the relation between physical and chemical soil properties and metal uptake by plants (Gough and others, 1980). This procedure resulted in prediction equations that related the concentration of a given element in plants to selected physical and chemical soil properties. The resulting prediction equations showed that diethylenetriamine-pentaacetic acid (DTPA) extractable levels were more important as a measure of the element-available soil fraction than ethylenediaminetetraacetic acid (EDTA) levels.

The parameter pH appeared in more of the regression equations than any other independent variable, and the regression coefficient was always positive. The standard partial regression coefficient ratios showed that, in those equations where pH occurred with other significant independent variables, pH was always the most

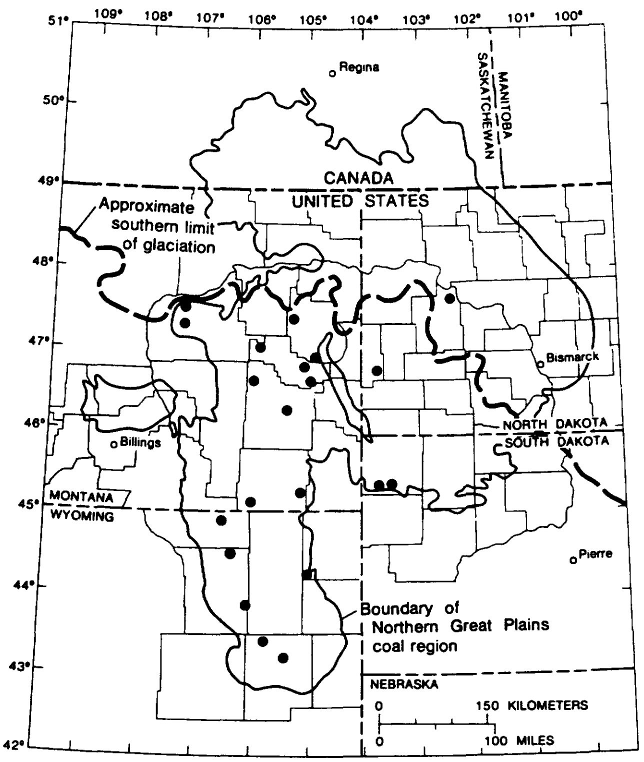

Figure 11.1. Sampling locations (dots) within the area of strippable coal deposits, northern Great Plains.

important. In general, copper, iron, and zinc concentrations in native plants increased with increasing pH of the A horizon (pH range of 6.2–8.2). Further, as pH of the A horizon increased, so did the relative uptake of these three metals. It is theorized that, below a pH of about 7.5, these metals exist mainly in noncarbonate forms but that, above a pH of 7.5, they also occur as metal carbonates. Therefore, a slight reduction in pH in the rhizosphere (caused by acid production at the root surface) could easily release metals from these carbonates in ionic forms readily available for assimilation by wheatgrass. These data suggest that native plants in the northern Great Plains tend to assimilate higher concentrations of copper, iron, and zinc when growing in A-horizon carbonate soils that have a pH above 7.5.

MINE-SITE METAL UPTAKE BY PLANTS

Mine-soil and plant-element relations.—A map of mines studied is given by Severson (fig. 24.1, this volume). A general lack of significant relations was found between the DTPA-extractable metal levels measured in mine soils and metals in plants. As with the native site studies, this lack suggests that a simple model is not adequate for estimating element uptake by plants. Organic-matter content and pH of mine soils, individually or in combination with DTPA-extractable metals, do not adequately model plant-element uptake from the mine soils in this study. Positive relations between the relative uptake of DTPA-extractable metals in mine soils and pH are the same as those reported in the previous section for native plants growing on undisturbed soils.

Biogeochemical comparisons among mines.—Element concentrations were determined in samples of crested, slender, and intermediate wheatgrass, alfalfa, and fourwing saltbush (Gough and Severson, 1983). Differences in element concentrations of these materials were assumed to reflect variability in the mine environment, specifically cover soil and spoil mineralogy, lithology, and bioavailability. Comparisons of element levels were made among species from different mines and among species within mines. Mines were then ranked according to similar biogeochemical element amounts. Absolute concentrations of environmentally important elements were examined for possible phytotoxic levels. As an example, extremely high boron concentrations in saltbush at a Wyoming mine (110–610 ppm, dry material) reflected phytotoxic levels in the mine soils.

RECOMMENDATIONS

Studies are needed to develop a soil extractant that makes use of new information on the probable major mode of metal occurrence in soils and on the apparent role of metal carbonates as a prime reservoir for the direct assimilation of metal by plants. Investigations on mineral weathering as it relates to element dissolution would also help in the formulation of a new extractant. Although our work has resulted in prediction equations for metal uptake by plants (using various soil-chemical and physical parameters on both native and mine-disturbed sites), a satisfactory level of precision for these equations, compared to what might be obtained by a new extractant, has not yet been achieved. Additional work is needed to define baseline element concentrations in plant species used in mine rehabilitation. The U.S. Geological Survey is one of the few organizations that has approached such studies on a regional scale.

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12. Remote Sensing of Vegetative Responses to the Environment

By Nancy Milton

INTRODUCTION

Studies of geology and soils can be hampered by a vegetation canopy that obscures outcrops and covers soils with a thick layer of plant litter and humus. Biogeochemical and geobotanical techniques, however, have proved to be successful in deriving information about rocks and soil from vegetation characteristics. For studies requiring a broad regional perspective, and in areas where sampling is difficult, remote sensing of plants can provide a rapid, inexpensive means of assessing the chemical and physical environment in which the plants are growing.

PLANT RESPONSES TO ENVIRONMENT

The vegetation growing in a given area is adapted to the conditions of water, soil, and air that control growth. The response of the vegetation to anomalous conditions, such as the introduction of toxic elements (whether natural or cultural), can result in macroscopic or spectroscopic changes. For example, on a macroscopic scale, the growth of the plant can be stunted (dwarfism or decreased biomass) or enhanced (gigantism or increased biomass); the timing of flowering, fruiting, or senescence can be altered (phenologic changes); or the anomalous area may be invaded by different species better adapted to the presence of toxic levels of specific elements (such as the endemic flora associated with copper or the vegetation adapted to high magnesium-to-calcium ratios, or high nickel or chromium on ultramafics). Other responses are spectroscopic in scale and are not readily discernible. The uptake of toxic elements by plants can result in subtle changes in the spectral reflectance of leaves in the visible and near-infrared regions of the electromagnetic spectrum.

REMOTE SENSING OF VEGETATION

The vegetation responses that are visible to the eye frequently occur on a scale that allows remote detection by low-resolution satellite sensors. Changes in species distribution due to biogeochemical anomalies in the soil have been recorded in Landsat multispectral scanner (MSS) data. Phenologic changes, such as delayed leaf flush and early senescence in deciduous forests growing on mineralized soils, have been detected in Landsat Thematic Mapper (TM) data.

The spectral responses of vegetation that are not always visible to the eye can be detected by high-resolution sensors, presently limited to airborne platforms. Spectral responses of interest in geobotany occur in the region of the EM spectrum from 0.4 to 2.5 μm (fig. 12.1). These spectra of red maple and loblolly pine were recorded on a laboratory Beckman 5240 spectrophotometer, which uses an integrating sphere and a barium sulfate standard. Resolution is 1 nm between 0.4 and 0.8 μm and between 0.8 and 2.5 μm.

Low reflectance in the visible region (0.4–0.7 μm) results from absorption by plant pigments, notably xanthophylls and carotenoids in the blue and chlorophylls in the red region. Plants reflect about 40 to 60 percent of incoming radiation in the very near infrared (0.7–1.0 μm); this reflectance helps to prevent overheating. Reflectance in this region is controlled by scattering at interfaces between cell walls, air, and water. In the shortwave infrared (1.0–2.5 μm), reflectance decreases because of the presence of water to a low of about 5 percent.

The presence of toxic elements in the plants can result in changes in various regions of the plant spectrum. Of particular importance is the shift in the longwave edge of the chlorophyll absorption band centered near 0.68 μm toward shorter wavelengths. This shift is illustrated in figure 12.2, especially in the first derivative spectrum, which shows the change in wavelength position of the inflection point. The shift is variously reported in the literature to range from 6 to 20 nm in extent, so that high-resolution instruments are required to detect it. Field studies using airborne radiometer data have verified that such a shift takes place in the vegetation growing over geochemically anomalous soils in Montana, North Carolina, and Vermont.

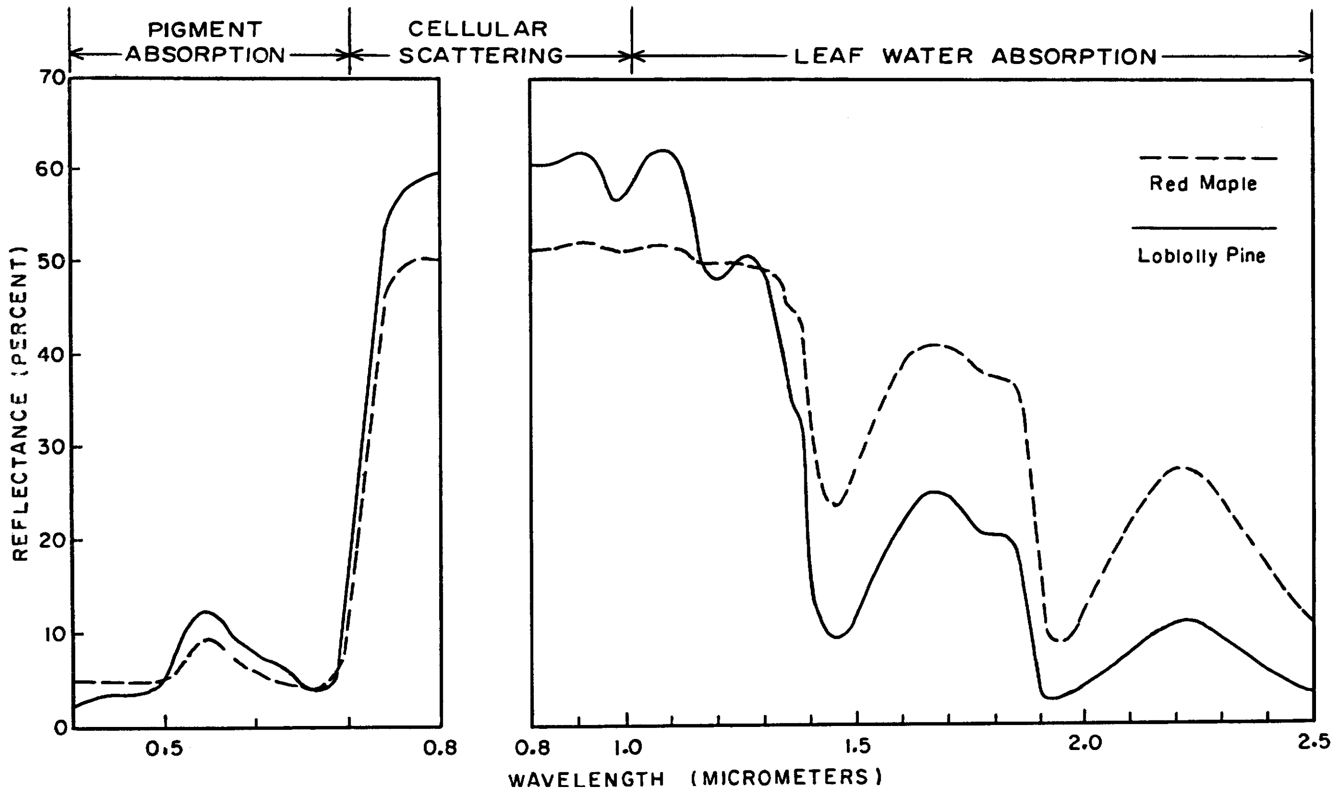

Figure 12.1. Spectral reflectance measurements of greenhouse-grown red maple and loblolly pine trees.

In summary, the remote-sensing capability exists at several levels of resolution to monitor plant responses to environmental conditions, such as the presence of geochemical anomalies in the soil.

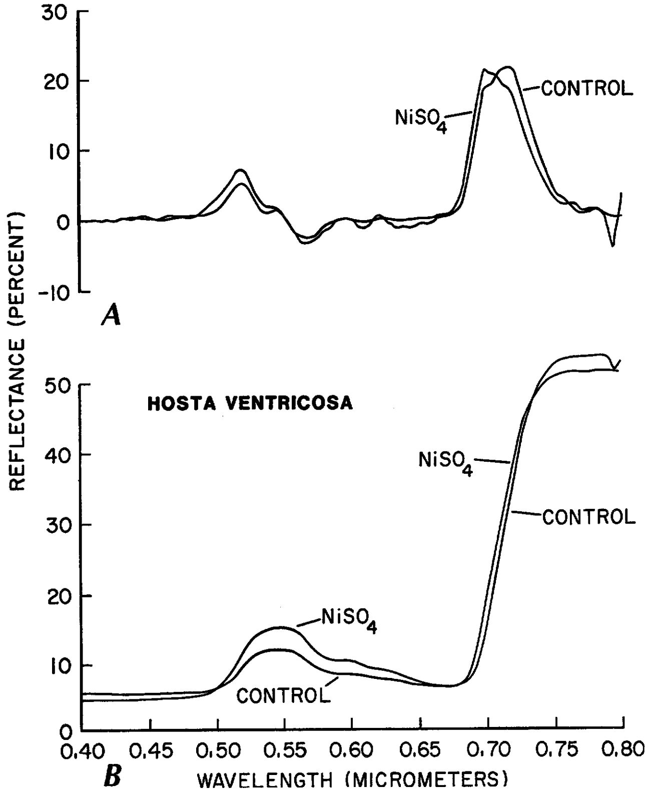

Figure 12.2. *A*, Spectral reflectance curves of $NiSO_4$-stressed and control hosta plants. *B*, First-derivative spectra.

13. Cooperative Studies by the U.S. Geological Survey and the U.S. National Park Service in Environmental Biogeochemistry

By Larry P. Gough, R.C. Severson, *and* Larry L. Jackson

INTRODUCTION

In July 1983, the U.S. Geological Survey (USGS) and the U.S. National Park Service (NPS) signed an interagency agreement for joint investigations of suspected biogeochemical problems originating from airborne contaminants in and near selected national park units (fig. 13.1). The NPS is responsible for protecting the air quality of park regions from significant deterioration. The USGS and the NPS are assessing the effect of known contamination sources on sulfur and trace-metal concentrations in plants, soils, and other natural materials (Gough, Peard, and others, 1985). Results of these studies are used in air-quality management decisions for the park units and for areas adjacent to them.

Study designs and specific objectives differ from one region to another and include (1) the use of lichens (or other "air plants") or vascular plant species as biomonitors of possible phytotoxic conditions, (2) the use of native materials to determine the region of measurable influence of a suspected point source of sulfur and (or) metal contamination, and (3) the establishment of baseline biogeochemical and geochemical levels so that the magnitude of chemical changes with time can be monitored.

SUMMARY OF COMPLETED STUDIES

Theodore Roosevelt National Park.—Investigations at Theodore Roosevelt National Park (TRNP), N. Dak., were divided into three parts: study 1, the comparison of lichen sample-preparation techniques and the development of a routine analytical method for the determination of sulfur in plant materials (Jackson and others, 1985); study 2, the definition of element-concentration baselines for selected plants and soils within TRNP; and study 3, the assessment of the influence of emissions from a natural-gas processing facility near TRNP on element levels of selected plants and soils (Gough, Peard, and others, 1985).

Samples of green ash, western wheatgrass, big sagebrush, a tree lichen, and soils were collected to estimate the areal biogeochemical and geochemical variability. Element-concentration baselines for plant species and soils were then estimated for TRNP. Extensive sampling was not necessary to establish the baselines because the concentrations of most elements in the materials sampled at random locations were fairly uniform. The data should be useful in future studies when the chemistry of new samples, collected, prepared, and analyzed in the same manner as in this study, are compared with the baseline values. Further, a comparison of total-element concentration levels in the materials sampled with published values of toxicity thresholds for trace elements and sulfur indicates no current instances of phytotoxic or zootoxic conditions in the park.

Of the elements determined in three plant species and soils collected downwind of a natural-gas processing facility near TRNP, only sulfur in tree lichen, boron in clubmoss, and sulfur in soil showed important inverse relations between concentration and increasing distance from the facility. Emissions from this facility were found to affect sulfur and boron levels up to about 4 km from the source.

Everglades and Biscayne National Parks.—The study was designed to measure the relative importance of sulfur and trace-element emissions, from the oil-fired Turkey Point electrical power generation facility in south Dade County, Fla., on nearby vegetation. The purpose was to distinguish between anthropogenic and natural sulfur and trace-metal sources and to estimate the zone of measurable influence of the powerplant emissions (Gough, Jackson, and others, 1985). The zone of measurable influence of the powerplant could not be precisely defined by utilizing principally plant material collected along four traverses in the study area. This geographic region has an extremely complex set of ecosystems, and even though the operation of the powerplant has had some effect on the sulfur chemistry of nearby materials, a major regional influence could not be demonstrated. Levels of Al, Co, Cr, Cu, Ni, V, and Zn in vegetation do not markedly decrease with

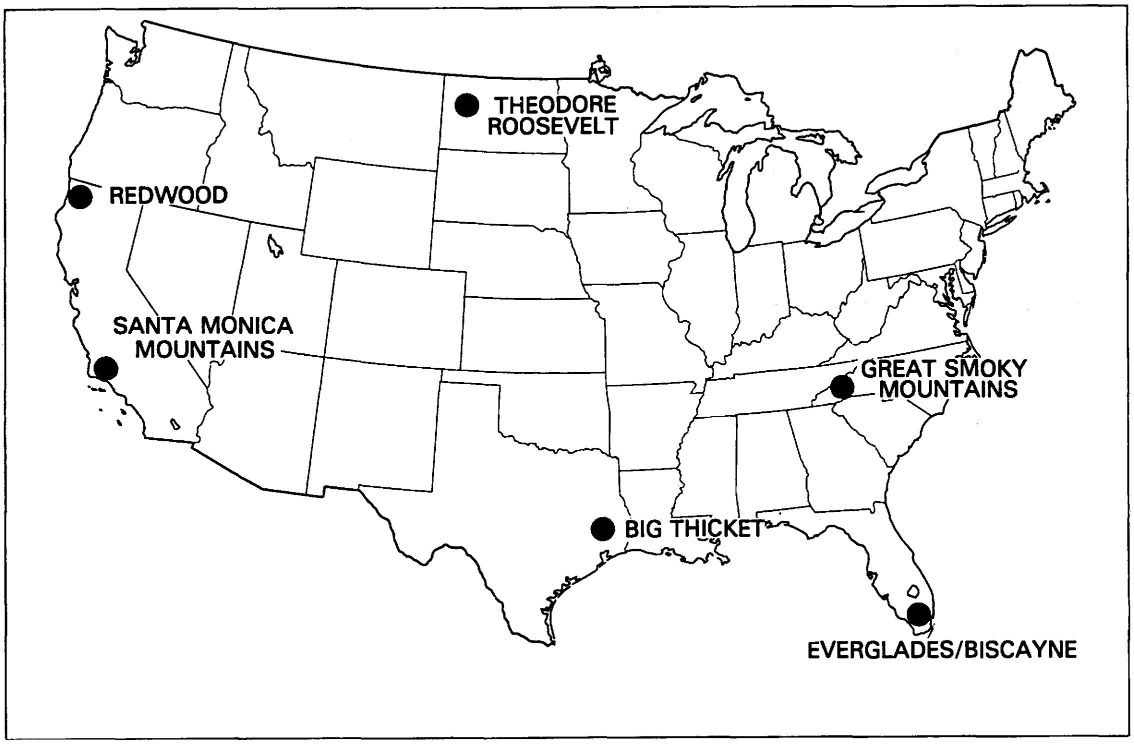

Figure 13.1. Past and present national park and recreation units investigated under the U.S. Geological Survey and National Park Service Cooperative Environmental Biogeochemistry project.

increasing distance from the powerplant. The trace-metal data suggest, however, a shadow effect within 1 km of the emission stacks.

Of the metal concentrations measured, only lead and sodium levels in plant materials might be considered large but not unusually so. Our results show a measurable marine influence, which helps explain the values for sodium. These values are fairly typical for coastal regions. Lead, on the other hand, is such a ubiquitous anthropogenic metal that multiple industrial sources are undoubtedly involved in its biotic concentration and distribution.

The relative abundance of stable sulfur isotopes in vegetation helped discriminate the sulfur in vegetation that is being contributed by the sea from that which is being contributed by the operations of the powerplant. Samples of fuel oil from the powerplant possessed $\delta^{34}S$ values equal to about zero per mil, and the only similar $\delta^{34}S$ values in vegetation were found at a site about 1 km from the powerplant. Marine sulfate has a $\delta^{34}S$ value of about +20 per mil. Larger positive $\delta^{34}S$ values of samples collected elsewhere near the coast apparently reflect the addition of marine sulfate.

Redwood National Park.—Redwood National Park (RNP) in northern California is close to vast lateritic nickel deposits. The proposed mining and milling activities at Gasquet Mountain will become a source of SO_2 and airborne metals. This source is expected to emit several hundred tons of SO_2 per year and an unknown, but potentially significant, quantity of trace metals, specifically Cr, Ni, Co, Fe, and Mn, which are all of environmental and biological importance. These emissions may have a direct local influence on the flora of the region. Tree lichens are known to concentrate metals and are also sensitive to elevated SO_2 levels. By measuring the background level of sulfur and metals in common lichen species before development of the resource, it will be possible to assess the potential for harmful SO_2 impacts and to monitor any increase in the trace-metal burdens in lichen tissue. This latter parameter would help signal the need for more detailed element cycling studies.

SPECULATIONS AND RECOMMENDATIONS

With the continued development of lands near national parks, preserves, and recreation areas, there is both a legal and an ecological interest in the definition of the impact of suspected point sources of airborne contaminants. In accordance with the Clean Air Act, the NPS must monitor potentially toxic trace elements and sulfur so that an unacceptable deterioration of pristine air does not occur. The introduction of increased levels of sulfur into park regions not only will affect the growth and reproduction of susceptible plant species but also will upset sensitive food chains. Further, an increase in the acidity of lakes or soils may increase the mobility of heavy metals, potentially causing localized phytotoxic conditions. The NPS and the USGS have continued to express an interest in supporting studies that define baseline geochemical and biogeochemical studies in park regions that they have identified as likely to undergo continued or future elemental impact. The USGS occupies an enviable position for providing necessary data for decisionmaking because it is viewed as an impartial third party with a strong earth science and associated analytical chemistry reputation.

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14. Monitoring Geochemical Processes with Geophysics

By Gary R. Olhoeft

The movement of electrical charge in a variety of physical and chemical processes may be observed directly by electrical geophysical methods. The chemical processes include oxidation-reduction reactions at the surfaces of metallic minerals in contact with water, ion exchange with the surfaces of clays and zeolites, and a variety of clay-organic reactions.

By stimulating the Earth with an electrical current at varying frequencies and amplitudes and measuring the voltage response, these geochemical processes may be monitored by using the geophysical technique called complex resistivity. At a single frequency of measurement, the ratio of voltage to current multiplied by a geometric factor is the resistivity. The resistivity is a complex number having both magnitude and phase and may be nonlinear (Olhoeft, 1979a,b). In the absence of chemical processes and at measurement frequencies below 1,000 Hz, the phase angle and nonlinear parameters of the complex resistivity are all very small numbers (ideally zero). As chemical processes become active, the phase and nonlinearities increase.

The spectral shape of phase and nonlinearity versus frequency produces diagnostic indicators of the type of chemical process: barren, redox, ion exchange, or clay organic. Examples of these complex resistivity signatures have recently been reviewed by Olhoeft (1985). These measurements may be made in the laboratory (Olhoeft, 1979a,b, 1985), in the borehole (Olhoeft and Scott, 1980), or from the surface of the Earth (Sumner, 1976; Olhoeft, 1984). By varying the geometry of the electrode array, the volume of investigation may be altered to produce a three-dimensional picture of the geochemical activity.

In Henderson, Nev., the separation of inorganic from organic components in a plume leaking from an industrial site was measured by complex resistivity. The inorganic component of the plume lowered the resistivity. The organic component of the plume depressed the normal phase response of the clays present at the site. The complex resistivity data showed that the inorganic components were contained above a clay aquitard, whereas the organic components had penetrated into the clay aquitard. Wenner array surface soundings, borehole electrical logs, and laboratory measurements on core samples having complex resistivity all agreed remarkably well (Olhoeft, 1984).

In Willow Springs, La., leakage from a landfill was measured by complex resistivity. Again, the inorganic portion of the plume was detected by a decrease in resistivity, and the organic portion was detected from a clay-organic reaction visible in the phase response. However, the character of the complex resistivity signature in Willow Springs was very different from that observed in Henderson. Figures 14.1 and 14.2 illustrate laboratory measurements on core samples from Henderson and Willow Springs, respectively. Note the phase differences between the contaminated and uncontaminated samples (for further details, see discussion of figures in Olhoeft, 1985). More laboratory work is required to identify the difference in the mechanisms between the two sites.

The complex resistivity technique is slower and more expensive than the loop-loop electromagnetic induction technique. Loop-loop electromagnetic induction can map the location of resistivity anomalies caused by inorganic contaminants. Organic contaminants produce very small resistivity changes compared to the inorganic contaminants and are thus often masked by the presence of inorganic components. Only the complex resistivity technique can independently observe organic components reacting with clays. However, the complex resistivity technique cannot detect organic components that do not have clays. When clays are absent, ground-penetrating radar has a higher probability of detecting organic contaminants because of the contrast in dielectric permittivity between organic contaminants and soil-water systems.

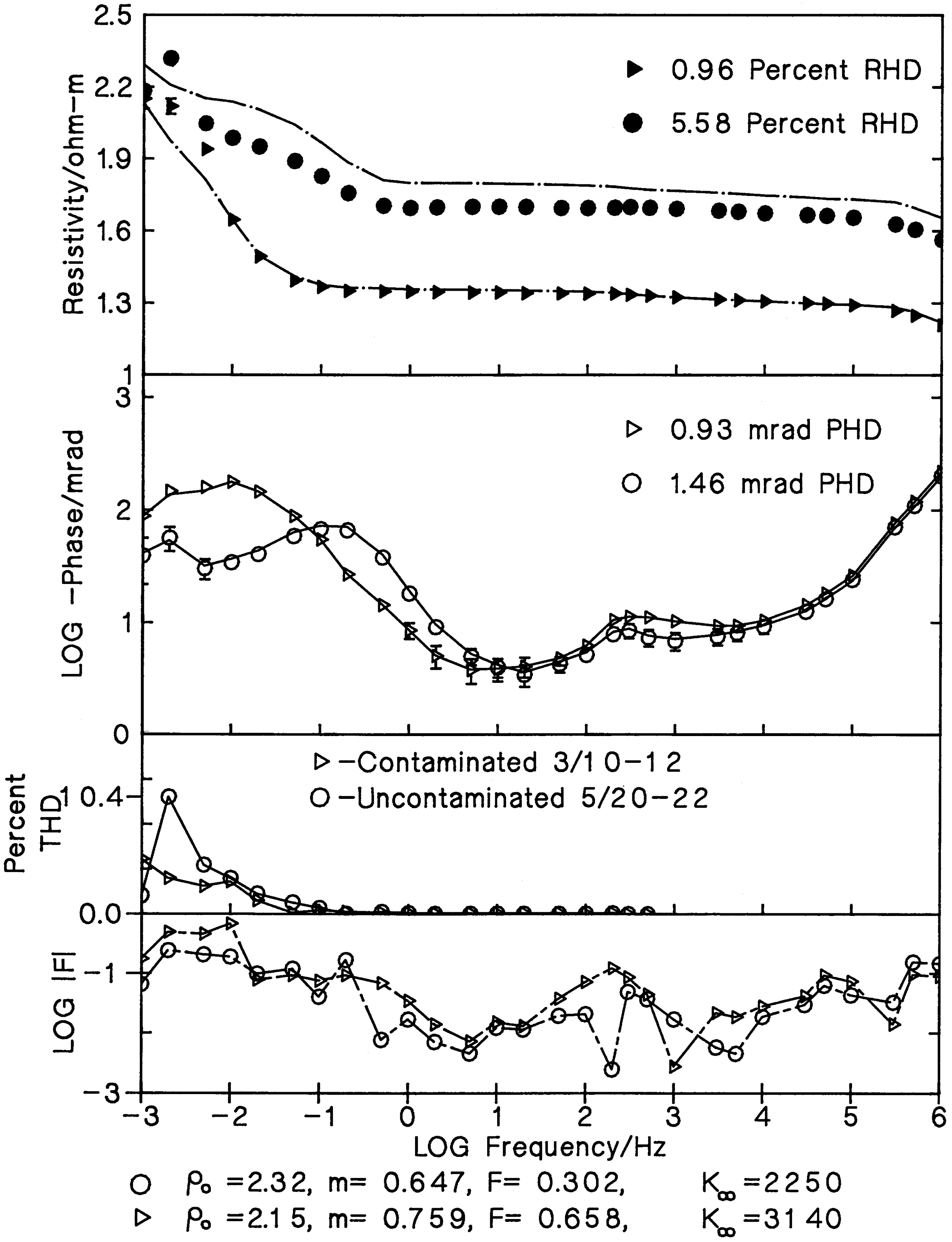

Figure 14.1. Complex resistivity spectra of montmorillonitic clay soil from Henderson, Nev., uncontaminated (circles) and contaminated (triangles) with organic waste from an industrial site. The shift in phase to lower frequency with contamination indicates inhibition of the cation exchange process by the organics. RHD, resistivity Hilbert distortion. PHD, phase Hilbert distortion. THD, total harmonic distortion. F, Faradaic time constant distribution normalization factor. |F| Faradiac time constant distribution remapped into the frequency domain. σ_o, DC resistivity in ohm-m. m, volume chargeability. K∞, high-frequency relative dielectric permittivity. See Olhoeft (1985, fig. 17) for a detailed explanation.

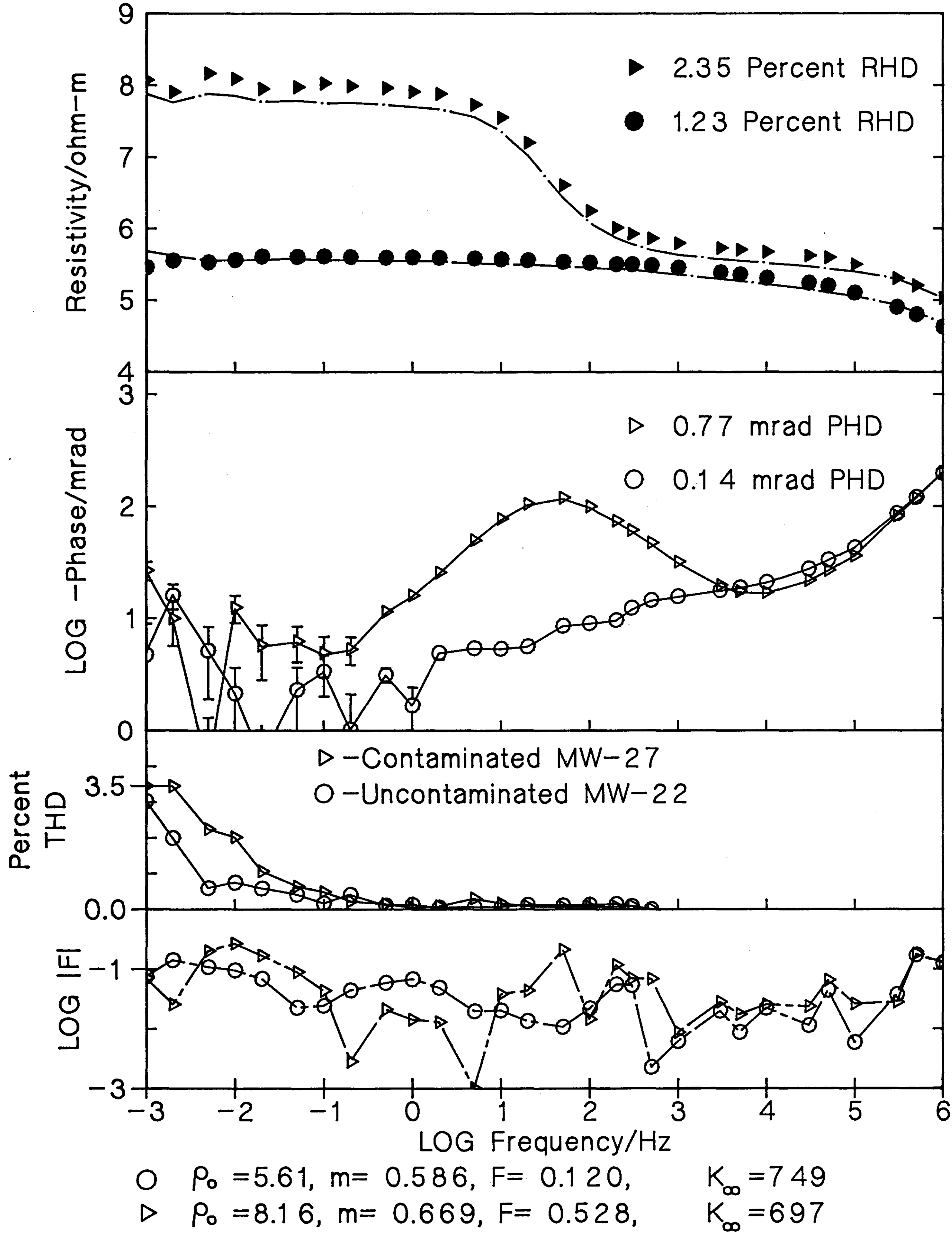

Figure 14.2. Complex resistivity spectra of clay soil from Willow Springs, La., uncontaminated (circles) and contaminated (triangles) with organic waste from a leaking landfill. In contrast to figure 14.1, the organic in this case probably is toluene, which interferes with charge movement between clay particles (Sadowski, 1988), in effect altering the way the clay particles "see" each other. See the caption of figure 14.1 for symbol definitions and Olhoeft (1985, 1986) for a detailed explanation.

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15. Bedrock Geochemistry and the Environment

By Jon J. Connor

Bedrock geochemistry for the most part only indirectly influences the quality of the human environment, largely because a complex surficial cover (soils, plants) prevents much direct human contact with rocks (fig. 15.1). Even so, sedimentary rocks, which constitute perhaps 75 percent of the near-surface bedrock in the conterminous 48 States, do play an important role in two specific areas of environmental interest; they may control the chemistry of potable water supplies, and if exposed at the surface in large amounts (by mining, for example), they may drastically alter the surficial geochemical environment.

The impact of reservoir rock on ground water, largely through pH control of metal content, can be of prime importance. Naturally soft water (low pH) tends to be higher in many trace metals than hard water (high pH), and much attention has been given to the possible role of hard and soft water in the etiology of heart disease in this country (Schroeder, 1960). The surficial effects of coal mining or metal ore extraction may easily result in the introduction of high concentrations of metals into the surface environment. As an example, chronic molybdenosis in cattle on a ranch in central Missouri was apparently induced by weathering of (and consequent metal transport from) a clay-pit spoil pile upstream of the ranch (Ebens and others, 1973).

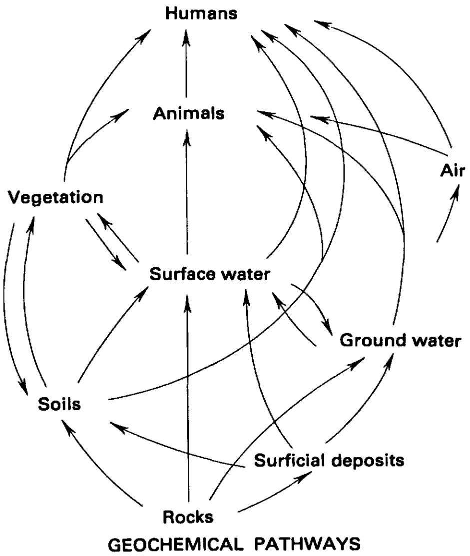

Figure 15.1. The role of rocks in influencing the near-surface geochemical environment.

A knowledge of elemental abundances in sedimentary rocks is, therefore, important to geochemical studies of the surficial environment. However, little more has really been learned about trace-element concentrations in such rocks since the work of Turekian and Wedepohl (1961). Their summary of element abundance in sandstone, shale, and carbonate rock is widely accepted as the standard against which geochemical change or anomaly in the surficial environment is measured. The relatively narrow base on which their estimates were made and the wide compositional variation within the three classes of sedimentary rock, however, should give one pause if these estimates are used to evaluate local geochemical anomalies in the surface environment.

Of the sedimentary rocks, shale is richest in most trace elements; estimates of expected metal content in shale are given in table 15.1. The first row lists the estimates of Turekian and Wedepohl. The second row gives estimates for a well-known organic-rich shale of Late Devonian to Early Mississippian age in Kentucky; such shales are known to be geochemically anomalous when compared to ordinary shales, but they may nonetheless constitute the norm in local areas. The third row lists estimates for a weakly metamorphosed (greenschist facies) shale of Middle Proterozoic age in western Montana, and the last row gives estimates for shale of Late Proterozoic? to Early Cambrian? age in the Western United States.

Consistency among the estimates ranges from good to bad. For example, the estimates in barium range from 510 to 620 parts per million (ppm) and for cobalt from 8 to 19 ppm, but ranges among the other elements are much broader. Molybdenum in black shale is high by a factor of about 25 compared with expected values of molybdenum in the other units, and manganese in black shale is low by a factor of about 6 or more. A wide disparity is seen in lead and copper, even if the copper-rich black shale is excluded. Incidentally, the shale having an expected concentration of 5 ppm copper is a "copper-shale"; that is, the unit contains copper deposits.

Table 15.1. Estimates of expected metal concentration in shale

Unit[1]	Element (in parts per million)					
	Barium	Cobalt	Molybdenum	Manganese	Lead	Copper
1	580	19	2.6	850	20	45
2	510	8.1	72	65	23	130
3	620	12	<2	380	10	5
4	510	13	<4	420	<3	14

[1] Unit 1—Shale, unrestricted (Turekian and Wedepohl, 1961); Unit 2—Chattanooga, Ohio, and New Albany Shales in Kentucky (Connor and Shacklette, 1975); Unit 3—Spokane, Grinnell, and St. Regis Formations in northwest Montana (J.J. Connor, unpub. data); Unit 4—Sauk sequence in Western United States (Connor and Shacklette, 1975).

The point of these comparisons is not to argue that some estimates are better than others, but rather to argue that wide (and legitimate) differences exist in estimates of expected concentration in lithically similar bedrock. Turekian and Wedepohl's estimates are of worldwide (crustal) application and are subject to unknown error, to which these authors freely admit. The remaining estimates, each representing a coherent stratigraphic unit within a known geologic setting, pertain to well-defined units of lesser, but still regional, extent. Estimates in these smaller units (rows 2, 3, and 4, in table 15.1) are clearly superior for evaluating anomalous surficial geochemistry in their respective areas of subcrop, but they are more costly to produce. The wide scatter in the estimates illuminates the magnitude of effort in field and laboratory work, which is needed if serious evaluation of the geologic substrate as a trace-element source to the surface environment is to be continued.

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16. Geochemistry of Rock-Water Reactions in Basalt Aquifers of the Columbia River Plateau

By Paul P. Hearn, Jr., William C. Steinkampf, Lloyd D. White, *and* John R. Evans

INTRODUCTION

Understanding the interactions between ground water and aquifer materials is critical to any study involving the geochemistry of ground water; knowledge of mineral-water reactions can provide valuable information regarding the chemical evolution of ground water and often may give important insights into other hydrological processes. This report summarizes the results of a geochemical and oxygen-isotope study of the basalt aquifers of the Columbia River Plateau. A conceptual model for the chemical evolution of Columbia River Plateau ground water is described on the basis of the composition and paragenesis of secondary phases and progressive changes in ground-water chemistry with increasing residence time in the system. Oxygen-isotope data are used to estimate the formation temperatures of secondary minerals and to place initial constraints on the timing of alteration reactions.

COLUMBIA RIVER PLATEAU

The Columbia River Plateau is a structural and topographic basin and has its lowest point near Pasco, Wash. The rocks of the plateau are primarily flat-lying flood basalts of Miocene age, which reach thicknesses of more than 1,500 m in the central part of the basin. The hydrologic system considered here is bounded on the north by the Columbia River, on the east by the Washington-Idaho border, on the south by the Blue Mountains, and on the west by a line midway between the Columbia River and the Cascade Range. The vertical and areal extents of the major aquifers were mapped by Drost and Whiteman (1986) on the basis of records from some 2,500 water wells within this area. Hearn, Steinkampf, Bortleson, and Drost (1985) described regional trends in ground-water chemistry and secondary alteration on the basis of ground-water data from 49 of these wells and on analyses of secondary alteration obtained from outcrops, drill cuttings, and core samples from the Hanford test site (fig. 16.1).

MINERALOGY AND PARAGENESIS OF SECONDARY ALTERATION

Secondary minerals in the Columbia River basalt tend to be concentrated in the fractured and vesicular zones in the bases and tops of individual basalt flows; these zones generally represent the major pathways of ground-water flow. Studies by Ames (1980), Benson and Teague (1982), and Hearn, Steinkampf, Bortleson, and Drost (1985) have shown that the most common secondary minerals include a smectite close to nontronite in composition, the zeolite clinoptilolite, iron oxide of indeterminate crystallinity, opaline silica, and quartz. Although other secondary phases are common, they occur mostly in minor or trace amounts.

On the basis of the sequence of alteration observed in vesicles and fractures, and vertical differences in the relative amounts of secondary phases, Benson and Teague (1982) proposed the following paragenetic sequence: clay (mostly nontronite)→clinoptilolite→silica and (or) clay. Hearn, Steinkamp, Bortleson, and Drost (1985) also found appreciable iron oxide intergrown with early smectite in samples above 1,000 feet.

Secondary alteration of the basalt appears to occur almost exclusively at low (<100 °C) temperatures by reaction with ground water. There is no evidence of any hydrothermal alteration. This conclusion is supported by the mineralogy of the alteration assemblage (Benson and Teague, 1982; Hearn, Steinkampf, Bortleson, and Drost, 1985) and by oxygen-isotope data (Hearn, Steinkampf, Burns, and others, 1985).

Volcanic glass is by far the most unstable phase in fresh basalt, due to its lack of crystal structure and extensive surface area (Jones, 1966), and for this reason is probably the major solid phase participating in reactions with ground water. By comparing analyses of fresh glass with analyses of early smectite and clinoptilolite, one can get a general idea of alteration reaction pathways (table 16.1). Early smectite is significantly enriched in iron and magnesium and depleted in sodium, potassium, and calcium relative to volcanic glass. The marked enrichment of smectite in magnesium probably reflects the contribution of this element from the dissolution of pyroxene. In the later clinop-

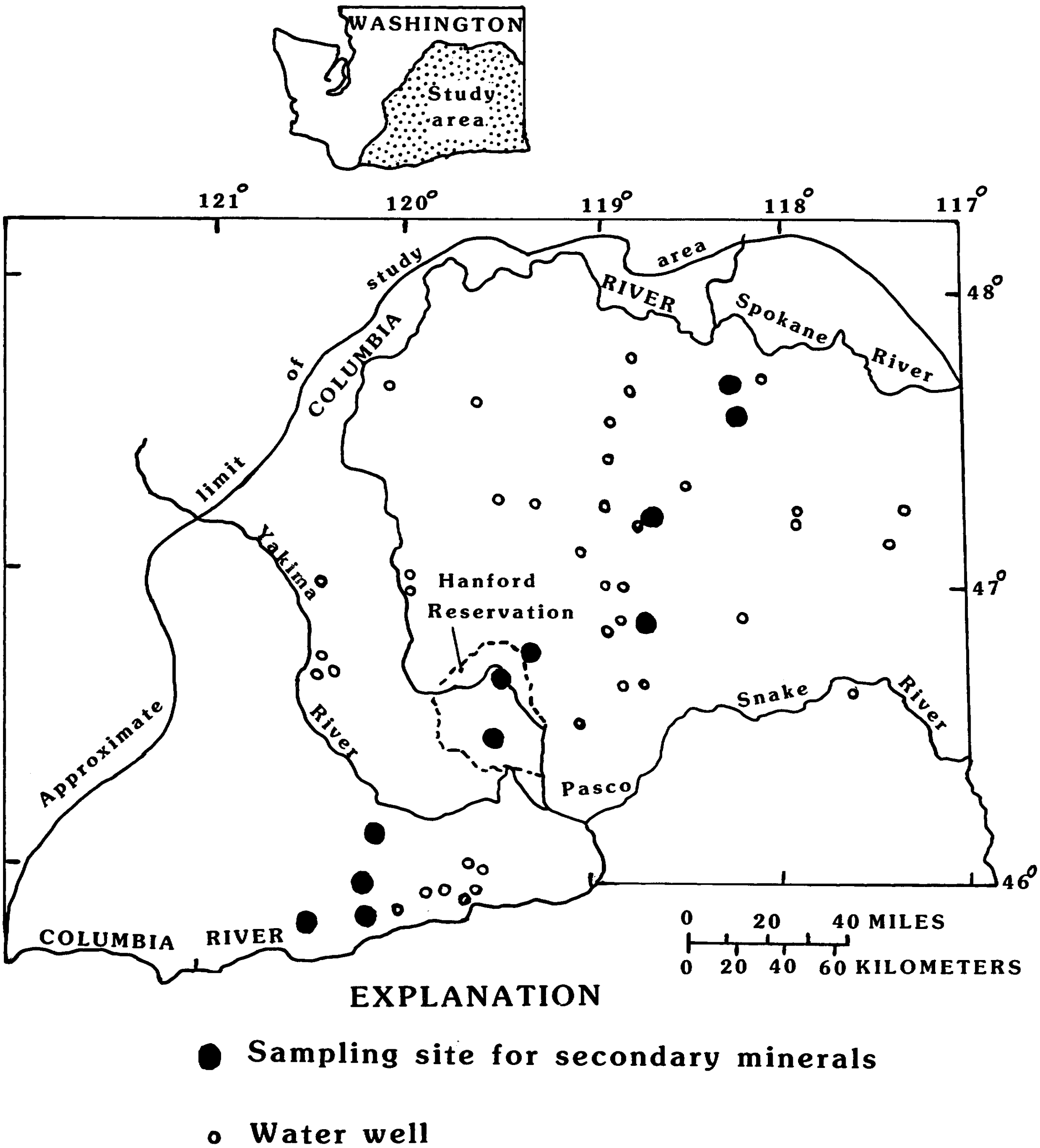

Figure 16.1. Study area in the Columbia River Plateau showing location of water wells and sampling sites for secondary minerals.

Table 16.1. Compositional variation during paragenesis

[Elements in weight percent; data normalized on a water-free basis, analysis by electron probe and SEM/EDS]

	Silica	Iron	Sodium	Potassium	Calcium	Magnesium	No. of samples
Entablature glass[1]	30.0	6.1	3.5	2.2	2.6	0.3	60
Smectite[2]	29.2	9.8	1.1	.7	1.2	5.6	40
Clinoptilolite[2]	34.0	.4	4.2	2.2	1.1	.2	30

[1] Long and Strope, 1983.

[2] Hearn, Steinkampf, Bortleson, and Drost, 1985.

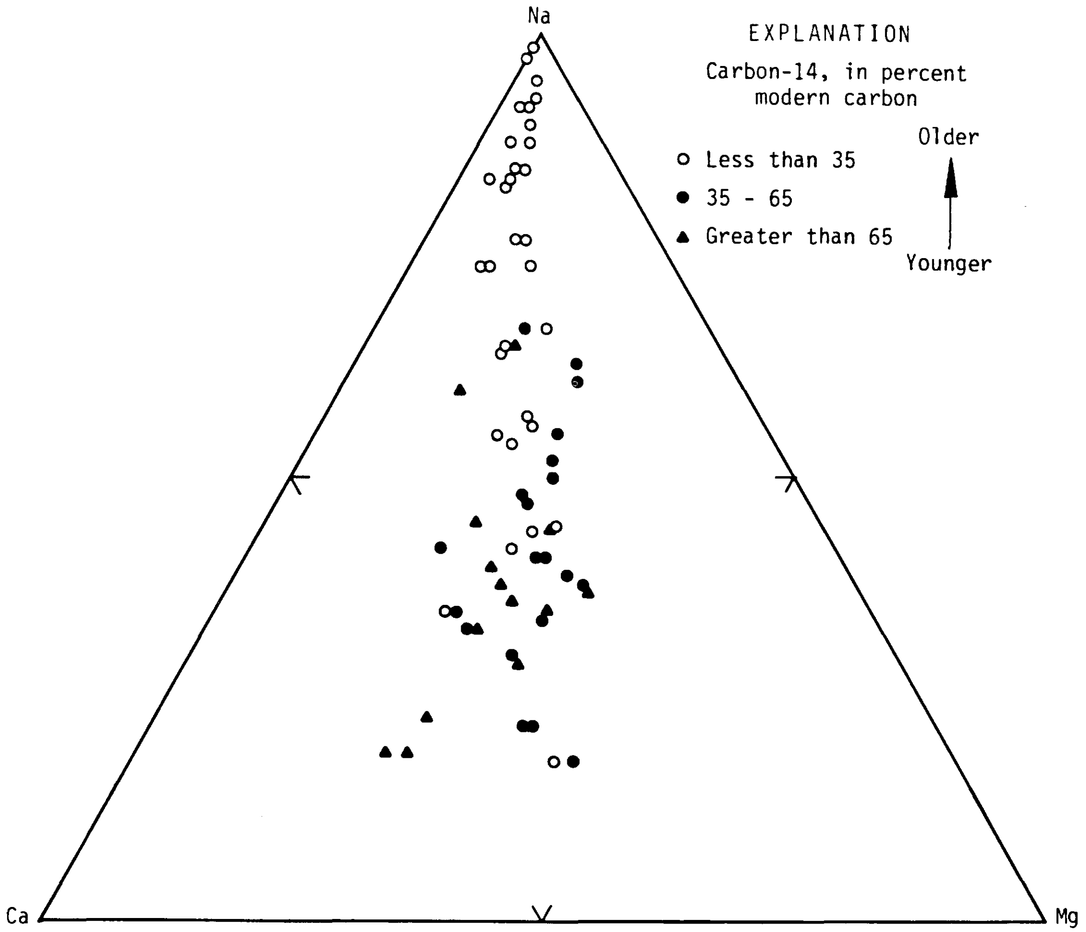

Figure 16.2. Molar plot of dissolved sodium, calcium, and magnesium concentrations in ground water, grouped in terms of relative age, Columbia River Plateau.

tilolite, the early trend is dramatically reversed; relative to the early smectites, the clinoptilolites are enriched in silica, sodium, and potassium and depleted in iron and magnesium.

CHEMICAL EVOLUTION OF GROUND WATER

Alteration reactions are also reflected by progressive changes in ground-water chemistry with increasing residence time in the system. A cation plot of dissolved sodium, magnesium, and calcium grouped in terms of relative ground water age shows a progressive enrichment of sodium with increasing age and a concurrent depletion of calcium and magnesium; the Ca:Mg remains fairly constant (fig. 16.2). Progressive trends are also apparent in several other constituents (fig. 16.3). Dissolved silica, potassium, and pH all increase with increasing residence time, whereas dissolved oxygen becomes progressively depleted. No corresponding trends are visible in the anion suite; bicarbonate is the predominant species in most samples (Hearn, Steinkampf, Bortleson, and Drost, 1985).

CONCEPTUAL MODEL OF ROCK-WATER REACTIONS

On the basis of the paragenetic sequence of secondary alteration and the progressive changes in water chemistry with increasing residence time, it is possible to construct a conceptual model describing the chemical evolution of ground water in the system. This model is similar in principle to the one proposed by Jones (1966). The primary reactants in the basalt are volcanic glass and pyroxene; plagioclase feldspar and iron-titanium oxides are thermochemically more stable and contribute substantially less material to solution (Jones, 1966; Benson and Teague, 1982). Dissolution proceeds primarily through hydrolysis; although CO_2 may participate in this process close to the ground surface, the generally thin soil cover suggests that its role is minor. The first solid products of this process are smectite and in some cases amorphous iron. Some evidence suggests that smectite may form by the gradual ordering of metastable amorphous compounds of silicon, aluminum, and other cations (Paces, 1978). As the hydrolysis reactions

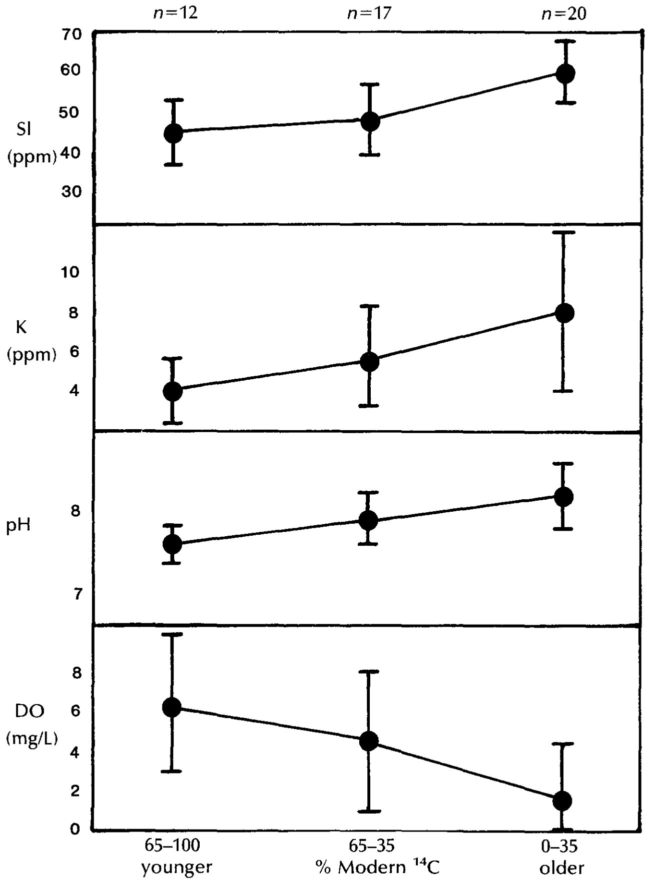

Figure 16.3. Average concentrations of dissolved silicon and potassium, dissolved oxygen (DO), and pH, plotted in terms of relative ground-water age, Columbia River Plateau. ppm, parts per million; *n*, number of samples.

proceed, the continued release of hydroxyl drives the pH upward and eventually precipitates calcite. Dissolved oxygen is consumed by the oxidation of ferrous iron in volcanic glass and pyroxene. In the early stages of alteration, silica, sodium, and potassium are all contributed to solution more rapidly than they are removed by precipitation, and the concentrations of these cations steadily increase. This process eventually produces alkaline ground waters supersaturated with clinoptilolite and silica, and these phases begin to precipitate.

OXYGEN ISOTOPE GEOTHERMOMETRY

Whereas abundant geologic and mineralogic evidence suggests that secondary alteration in the Columbia River basalt is a low-temperature phenomenon, the most convincing support for this contention is provided by oxygen-isotope geothermometry of secondary minerals.

Samples of vug-filling smectite, calcite, and silica were hand picked from surface outcrops, water-well drill chips, and drill core from test wells at the Hanford test site (fig. 16.1). All samples were screened by X-ray diffraction (XRD) and scanning electron microscopy/energy-dispersive X-ray fluorescence spectroscopy (SEM/EDS) to ensure their purity, prior to isotopic analysis. Oxygen isotope data for ground water from within the test site were obtained from Early and others (1985).

Formation temperatures of secondary minerals were computed by using mineral-water geothermometric equations of Yeh and Savin (1977) for smectite, Clayton and others (1972) for silica, and O'Neil and others (1969) for calcite. Formation temperatures for each sample were computed by using the closest available ground water $\delta^{18}O$ values. The results of these computations are plotted as a function of depth in figure 16.4. The computed formation temperatures for smectite, calcite, and silica all increase with depth. A least-squares fit of the data yields a gradient of approximately 46 °C, close to the thermal gradient of approximately 40 °C/km observed at the test site today. The difference is largely a reflection of the data from points shallower than 600 m; formation temperatures for these samples fall consistently below the local thermal gradient, whereas formation temperatures for deeper samples are evenly clustered around the thermal gradient. This discrepancy, together with the large amount of scatter in these data, most likely is due to the fact that the secondary minerals precipitated from ground water having a different oxygen-isotope composition than present-day ground waters. These differences may be both random (due to small-scale flow heterogeneities) and systematic (due to unidirectional or secular changes).

These preliminary results support the contention that secondary alteration of the basalts is a low-temperature, as opposed to a hydrothermal, process. Furthermore, the congruity of the formation temperatures with the present-day thermal gradient suggests that the alteration assemblage formed after the emplacement of the greater part of the basalt sequence. This contention is consistent with the ages of the constituent basalt flows and with estimated rates of alteration in deep-sea basalts. Studies of midocean-ridge basalts (MORB) indicate that low-temperature alteration by seawater begins immediately after cooling; however, significant perturbation of MORB $\delta^{18}O$ values from primary magmatic values appears to require a minimum of 1 to 2 million years (Muehlenbachs, 1986). The Grande Ronde and Wanapum Basalts, which constitute over 90 percent of the vertical thickness of basalt at the test site, were emplaced within an interval of approximately 2 million years (14.5 to 16.5 Ma). Although seawater alteration data obviously cannot be applied directly to a freshwater system, these observations agree well with the contention that secondary minerals did not equilibrate isotopically with ground waters until the greater part of the basalt flows had cooled to ambient temperatures.

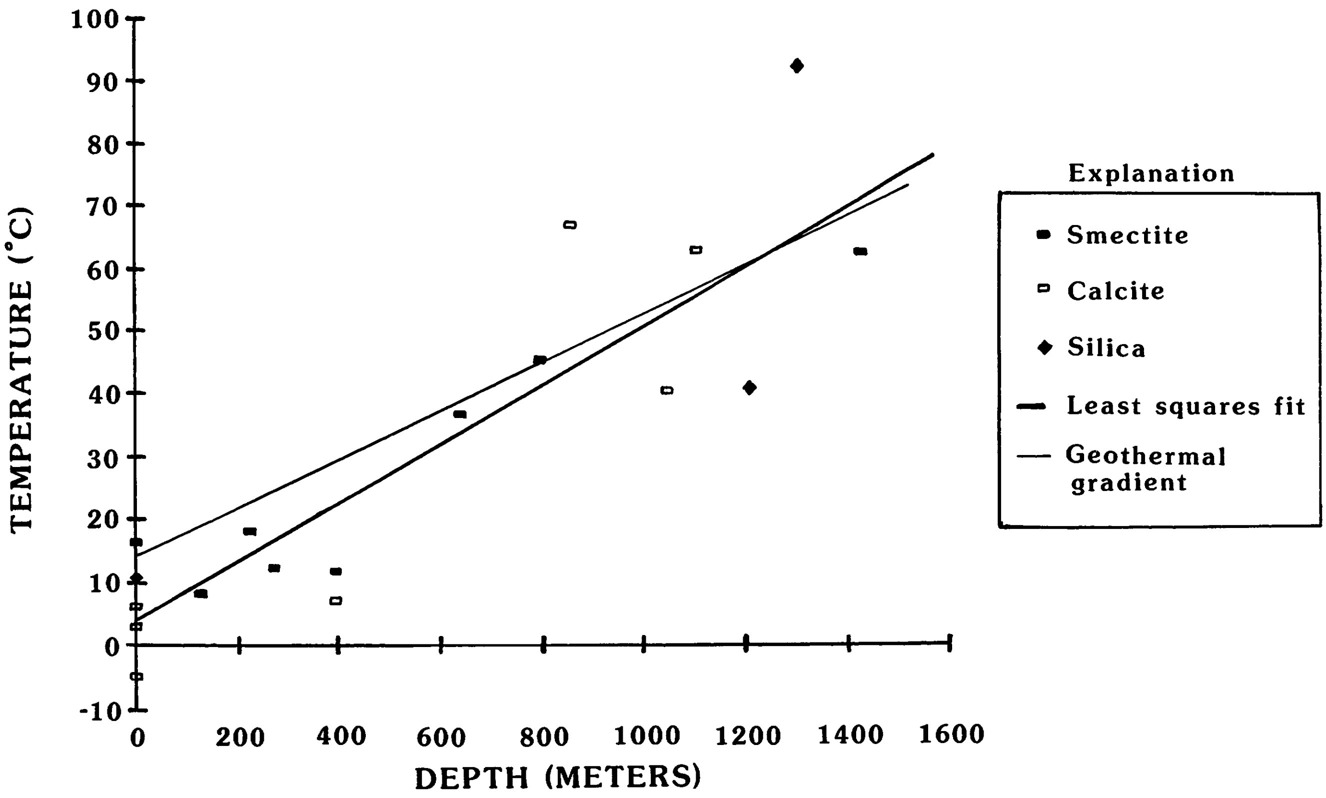

Figure 16.4. Formation temperatures computed by using in-situ $\delta^{18}O$ values.

CONCLUSIONS

The chemical evolution of ground water in basalt aquifers of the Columbia River Plateau is determined primarily by the hydrolysis of volcanic glass and pyroxene and the stoichiometry of secondary alteration products. This conclusion is supported by progressive changes in solute chemistry with increasing residence time and the composition and sequence of formation of secondary minerals. Ground water progressively evolves from a calcium-magnesium bicarbonate type in shallow upgradient sites to a sodium-potassium bicarbonate type in deeper downgradient sites.

Formation temperatures computed from oxygen-isotope analyses of secondary minerals indicate that alteration took place at temperatures roughly concordant with the present-day geothermal gradient of 40 °C/km. This relation suggests that secondary minerals did not equilibrate isotopically with surrounding ground water until the greater part of the total thickness of basalt (Grande Ronde and Wanapum Basalts) had cooled to ambient temperatures.

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17. Early Diagenesis and Metal-Organic Matter Interactions in Alkaline Playa Lakes of the Lahontan Basin, Nevada

By W.H. Orem

Playa or alkaline lakes form in basins or depressions isolated from the sea where evaporation exceeds freshwater input. The dissolved solids in the freshwater entering the lake are concentrated by evaporation, ultimately forming hypersaline and (or) alkaline conditions in the lake. Playa lakes have great economic importance as sources of minerals and metal ores and in some cases as areas of oil and gas formation. Also, studies of the geochemistry of natural playas may provide useful insight into toxic metal problems associated with reservoirs and irrigation in arid and semiarid regions. Despite this, playa lakes and evaporitic environments in general remain one of the most poorly understood biogeochemical systems on Earth.

This paper presents some very preliminary geochemical data on sediments and pore water from Carson Lake, Nev. The long-range objective of this project is to establish the processes involved in the early diagenesis of organic matter in playa lakes and the extent and significance of metal-organic matter interactions in these systems.

Carson Lake is a shallow playa (water depth of about 30 cm in August 1985) located near Fallon, Nev. This lake represents the terminus of the Carson River, which flows eastward from the Sierra Nevada Mountains. The lake is surrounded by a salt marsh and had a pH of about 9.5 at the time of sampling. Titration of the overlying and pore waters with 0.1 *M* HCl gave a titration curve having an inflection point at a pH of about 4.5. This curve is indicative of alkalinity in the lake dominated by bicarbonate and carbonate ions.

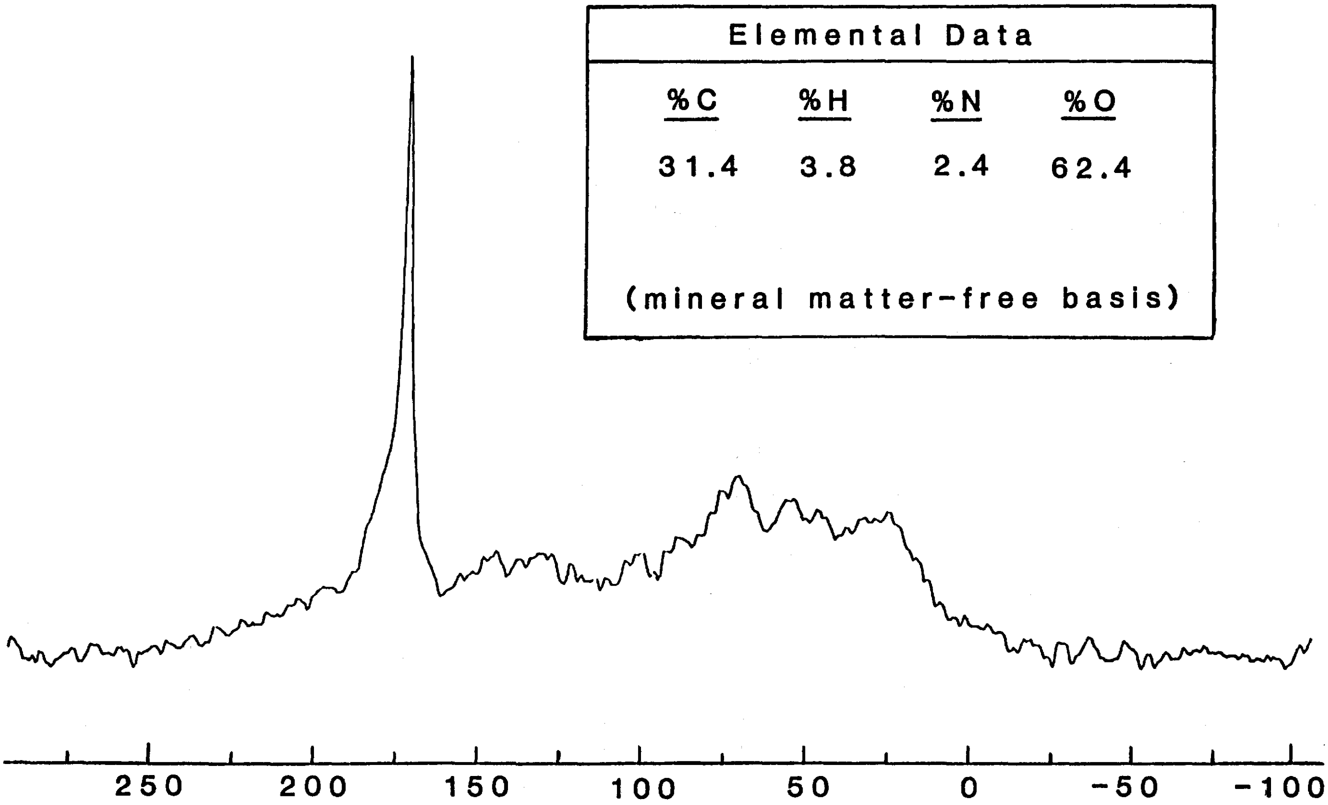
The sediment of the lake is composed of an organic-rich upper layer (2 cm depth) and a sticky clay below. The organic carbon data from an auger sample taken in the lake show a steady decrease in percent organic carbon with increasing depth (table 17.1). This decrease may indicate that the salt marsh surrounding the lake is a relatively recent feature or that organic matter deposited in the sediments is readily degraded or solubilized under the highly alkaline conditions present in the lake. Dissolved organic carbon concentrations in the pore waters are relatively high (about 100 mg/L of carbon). Thus, significant degradation (probably via sulfate reduction) and solubilization of the sedimentary organic matter are taking place.

One major goal of this preliminary study was to determine the gross chemical structure of the dissolved organic matter (DOM) in the pore water to evaluate its metal binding characteristics. This isolation of the DOM was accomplished by using ultrafiltration; its chemical structure, determined by using elemental analysis and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, is dominated by a peak at 175 parts per million (ppm); this peak is indicative of carboxyl and (or) amide carbons (fig. 17.1). The low nitrogen content (2.4 percent) and high oxygen content (62.4 percent) of the DOM, however, suggests that this peak must be predominantly due to carboxyl carbons. This finding, coupled with the unusually high atomic O:C of about 1.4 for this material, suggests that the DOM is composed primarily of multicarboxylic acids. This situation may be unique to alkaline lakes, because similar structures in the DOM have not been observed from a number of other sedimentary environments. This finding is significant, as di- and tricarboxylic acids are excellent binders of trace metals. I am pursuing this aspect of the overall study to obtain more detailed structural information.

Some preliminary data on the major- and minor-element composition of Carson Lake sediments are shown in table 17.2. The data suggest that little or no precipitation of typical evaporitic minerals is taking place in Carson Lake. The sediments appear to be composed of predominantly aluminosilicate clays that are probably highly altered

Table 17.1. Organic-matter composition of Carson Lake sediments

Depth (cl)	Carbon (percent)	Nitrogen (percent)
0–30	2.6	0.3
30–60	1.4	.2
60–90	1.6	1.0
90–120	1.8	.3
120–150	1.0	.9



Elemental Data

%C	%H	%N	%O
31.4	3.8	2.4	62.4

(mineral matter-free basis)

Figure 17.1. Elemental data and ^{13}C nuclear magnetic resonance spectrum of dissolved organic matter isolated from an alkaline playa lake, Carson Lake, Nev. ppm, parts per million.

Table 17.2. Major- and minor-element composition of Carson Lake sediments

[Measurements in percent, except as noted. ppm, parts per million]

Depth (cm)	Si	Al	Fe	Ca	K	Mg	Na	Ti	Cu (ppm)	Zn (ppm)	Pb (ppm)
0–30	47.4	16.1	17.6	6.7	5.6	3.6	1.6	0.8	69.44	100.21	20.58
30–60	50.5	17.3	17.8	4.7	5.1	3.0	.7	.6	51.98	93.93	13.85
60–90	59.3	17.1	17.0	4.6	5.1	4.6	1.5	.7	48.64	95.45	13.08
90–120	47.7	17.2	18.1	5.2	4.9	3.6	2.4	.7	47.99	97.84	13.86
120–150	51.8	18.8	15.5	4.8	4.8	3.3	.9	.0	39.96	90.16	10.44

by reverse-weathering-type reactions. Iron concentrations are relatively high, possibly due to the formation of authigenic mineral phases. The copper, zinc, and lead concentrations are typical for modern lacustrine sediments but show an interesting decrease in concentration with increasing depth. This trend correlates with the decrease in organic matter content in the sediment with depth mentioned earlier.

In summary, early diagenetic processes in sediments from Carson Lake are generating DOM in the pore waters having a very unusual chemical structure dominated by carboxyl groups. Such structures are ideal for binding metal ions, and alkaline lakes such as Carson Lake may be ideal environments for undertaking studies of interactions between metals and organic matter.

18. The Role of Organic Matter in Weathering Processes

By R.K. Kotra

Of major importance to environmental geochemistry is an understanding of weathering processes and the types and rates of interaction among the many geochemical variables that influence weathering processes. The geochemistry of weathering has been extensively studied with emphasis primarily on the inorganic species. The role of organic matter during weathering has been studied in much less detail.

Dissolved organic substances may play an important role in the breakdown of primary minerals in a variety of environments. The concentrations of organic solutes in surface waters and deeper waters can influence the pH and the redox potential. Organic solutes also can serve as complexing agents to mobilize some major elements. The chief solutes appear to be organic acids. These can be low molecular weight acids such as the aliphatic mono- and dicarboxylic acids and the aromatic phenols or high molecular weight substances such as humic and fulvic acids.

Carothers and Kharaka (1978) and Kharaka and others (1985) showed that oil-field waters from the Texas Gulf Coast and the San Joaquin Valley of California can contain as much as 5,000 parts per million (ppm) carboxylic acids in the temperature range 80–200 °C. Carboxylic acid anions contributed 50–100 percent of the measured alkalinity especially in the 80–120 °C range. At higher temperatures, carboxylic acids are gradually destroyed by decarboxylation reactions. The nature and concentration of phenolic species present in oil-field waters are poorly understood. Preliminary estimates indicate that phenolic compounds constitute 5–10 percent of dissolved organic carbon (DOC) of the brines from the southern San Joaquin Valley (Surdam and Crossey, 1985).

The relation between organic acids and the preservation and (or) enhancement of porosity in sandstone and shale sequences in hydrocarbon reservoirs has been examined (Surdam and Crossey, 1985, and references therein). The organic acids are thought to be derived from thermal and catalytic decomposition of the kerogen (insoluble disseminated organic matter in sedimentary rocks) in the source rocks. An optimum diagenetic scenario for the preservation and (or) enhancement of porosity requires that organic-rich rocks be adjacent to potential reservoir rocks and requires a rapid evolution from organic-acid generation to hydrocarbon maturation.

Antweiler and Drever (1983) reported that the weathering of an upper Tertiary volcanic ash in Wyoming was controlled by the presence of soluble organic acids derived from vegetation and soil. Both higher molecular weight dissolved organic matter (for example, humic and fulvic acids), as well as small organic anions (for example, formate, acetate, and oxalate), were present in the waters that influenced weathering. The concentrations of Na, K, Ca, Mg, Al, and Fe correlated with DOC and followed an annual cycle that had a maximum in the spring.

Preliminary results from a study on the early diagenesis and metal-organic matter interactions in an alkaline playa lake indicate that the high-molecular-weight dissolved organic matter (DOM) has an unusual chemical structure (W.H. Orem, this volume). The material has a high atomic O:C and appears to be dominated by carboxyl functional groups.

In the cases cited above, the source of the organic acids was vegetation, soil, and kerogen. Understanding the nature and origin of these source materials is important to predict the results of chemical alteration of mineral matter. For example, kerogen is the most abundant form of fixed organic matter in the crust of the Earth. The chemical structure of kerogen is complex and poorly understood despite many years of investigation. One classification scheme divides kerogen into three types on the basis of atomic H:C and O:C (Tissot and Welte, 1984). Type I kerogen is rich is aliphatic structures and is characterized by high hydrogen content such as that seen in some algal deposits. Type III kerogen is rich in polyaromatic structures and oxygen similar to plants of terrestrial origin. Type II kerogen is of intermediate composition. The chemical structure of humic substances is also complex. Application of new analytical approaches has recently resulted in much additional information concerning their origin and structure (for example, Christman and Gjessing, 1983). Recent studies on the high molecular weight DOM in pore waters from sediments have shown that the structure of the DOM is strongly influenced by the environment in which it is formed (Orem and Hatcher, 1987).

An integrated approach to the study of the effects of organic matter on weathering requires characterization of dissolved organic species in waters, as well as of the parent organic matter. The nature and abundance of the parent organic matter may have a direct bearing on the type and quantity of organic acids that are active in a given setting. Furthermore, the role of organic bases has not been investigated. The organic solutes may exist for only short periods of time, but their influence on the composition of ground and surface waters is significant and in some cases may be the controlling factor.

The role of organic matter in weathering processes is best examined by field studies in conjunction with laboratory simulations of the production of organic weathering agents under differing conditions and the effect of these agents on various mineral groups. Any assessments of the role of organic species in weathering will also have to consider the role of inorganic species; thus it is important to determine the forms of the major and trace elements in soils and waters. The results of such combined organic and inorganic geochemical investigations will be useful in understanding the interaction between organic matter and toxic inorganic elements, the transport of naturally occurring toxic materials, and their cause-and-effect relation to plant and soil microbe communities.

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19. Application of Geophysical Methods to the Study of Pollution Associated with Abandoned and Injection Wells

By Frank C. Frischknecht[1]

INTRODUCTION

Contamination of ground-water supplies by brine and other pollutants is a serious problem in some oil-producing and industrial areas. Abandoned petroleum and water wells and active injection wells are often major elements in the contamination process. The casings of abandoned wells develop leaks, and, if not properly plugged, such wells sometimes serve as conduits for pollutants to reach freshwater aquifers. Pollutants from waste-disposal sites or accidental spills may migrate down abandoned wells. Brines or other wastes injected into deep horizons may migrate up abandoned wells and reach aquifers containing potable water. Injection wells sometimes develop leaks and, if not carefully monitored, can pollute large volumes of earth materials before the effect is noted in production wells or at the surface. As a first step in the mitigation of these problems, methods of locating abandoned wells and mapping brine contamination from injection wells have been studied by the U.S. Geological Survey in cooperation with the U.S. Environmental Protection Agency (EPA).

LOCATION OF ABANDONED WELLS

Pollution caused by abandoned or unknown wells is especially acute in regions where there are old petroleum fields or extensive agricultural areas that have been irrigated from water wells. In 1979, there were estimated to be as many as 1,800,000 producing, dormant, and abandoned wells in the United States (Federal Register, 1979). In local areas, the number of wells is as high as 2,000 per square mile. In the early days of petroleum production, the locations of wells were not always recorded. Available records are sometimes inaccurate, and, in some States, locations were recorded only in terms of land subdivisions such as quarter sections. In some older agricultural areas, systematic records of water wells were not kept. Therefore, there is a need for direct methods of locating abandoned wells.

Magnetic and geoelectrical methods were evaluated for use in locating abandoned wells. A few geoelectrical methods were found to be useful in special applications, such as mapping the buried horizontal pipelines that are often associated with wells (Frischknecht and others, 1983; Jachens and others, 1986). However, the magnetic method proved to be much more useful for most purposes.

In evaluation of the magnetic method, ground magnetometer surveys were made over several wells in two oil fields near Denver, Colo. Distinctive, monopolar-shaped anomalies having peak amplitudes of as much as several thousand nannoteslas (nT) were noted above the casings. The results were fit to appropriate pole-pair models by using a nonlinear least-squares algorithm. By means of the parameters determined from the ground data, modeling was carried out to determine suitable specifications for airborne measurements (Frischknecht and others, 1983). Airborne surveys were conducted over an oil field near Denver, Colo., and parts of four oil fields near Oklahoma City, Okla., to evaluate the usefulness of airborne surveys in locating wells. All of the surveys were made by using a flight height of 61 m and a flight-line spacing of 100 m. A ground transponder-based microwave navigation system was used to provide the position of the aircraft within a few meters (Frischknecht and Raab, 1984; Frischknecht and others, 1985).

Three independent sets of data were used in evaluating the effectiveness of the airborne surveys in Oklahoma—visual and ground magnetometer observations at selected sites, a compilation of information from records, and results of an analysis of aerial photographs. Ground magnetometer measurements were made at sites where there was no obvious visual evidence of a casing to determine if there were hidden casings. Fairchild (1984) conducted a records search to determine the locations and specifications of all known wells in the areas surveyed. The available records

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[1] Deceased.

did not give exact locations of wells, but they did provide estimates of the total number of wells in each section. Stout and Sitton (1984) identified probable locations of wells from analysis of several sets of aerial photographs taken at different times, the earliest set having been taken in the 1930's.

As an example of the results, an aeromagnetic contour map for part of Coon Creek field northeast of Oklahoma City is shown in figure 19.1. Forty distinct magnetic features are labeled on the map; all features except No. 1, which is a negative anomaly, are believed to be caused by a single well or a cluster of wells. In section 3, which encompasses most of the area of figure 19.1, the records search found 41 wells. The original photo analysis identified 36 probable wells in section 3, and the magnetic data indicate the presence of 39 wells. One well (I) was not detected by the airborne survey, probably because it occurs on the flank of a large anomaly (15, 15b) caused by other wells. Another such "hidden" well may account for the discrepancy between the results of the records search and the airborne results. A photographically identified well at III is not reflected in the contour map, but it caused distinctive anomalies of 4 and 5 nT in the aeromagnetic profiles along the nearest flight lines. One site, where there was a possible photographically identified well (II), was found not to contain a casing. The results for the Coon Creek field are fairly typical of all four test areas in Oklahoma. However, in most of the sections surveyed, the total number of magnetic anomalies that may be caused by casings exceeds the number found from records or estimated from aerial photographs. Magnetic methods should be equally effective in locating wells in other regions where conditions are similar to those in the Oklahoma test areas.

In the test area in Colorado, tuffite beds or other magnetic material in the near-surface rocks caused short-wavelength anomalies that interfered with identification of anomalies from wells. However, evidence of most of the known wells and of one unknown well was found through examination of the aeromagnetic profiles rather than the contour maps. Ground checking was required to verify some of the interpretations.

A pilot project was conducted in industrial and residential areas of Santa Clara County, Calif., to explore the feasibility of locating abandoned water wells from analysis of historical aerial photographs and ground magnetic measurements. In this region, wells that were used for irrigation of orchards and other crops have been abandoned and covered over, and they are, in part, responsible for migration of chemicals from industrial spills into aquifers used for water supplies. Measurements over known water wells in the area showed that these wells produce magnetic anomalies of several hundred nannoteslas or more at the surface. In rural areas, such wells could easily be located by closely spaced ground magnetic measurements. At three sites, where photointerpretation by K. Stout (oral commun., 1985) indicated the presence of wells, magnetic anomalies characteristic of casings were found. Characteristic anomalies were not found at six other photographically identified sites, possibly because the casings are gone. However, limited access to these sites due to buildings, streets, fences, and other urban structures and interfering magnetic anomalies from a host of steel objects including fences, lampposts, buildings, and automobiles made the use of the magnetometer difficult. Nevertheless, Jachens and others (1986) concluded that ground magnetic methods can be effective tools in locating some of the wells in an urban environment.

MAPPING BRINE CONTAMINATION

As part of an EPA research program on methods for detecting and mapping fluids leaking from injection wells, transient electromagnetic soundings were made at two localities near Pawhuska, Okla., where brines have contaminated the surface (Fitterman and others, 1986). Zones of intense brine pollution have lower electrical resistivities than unpolluted regions containing fresher water. At one of the two test areas, brine has seeped out at the surface along fractures apparently caused by overpressuring a nearby injection well. Locations of electromagnetic soundings at this area are shown in figure 19.2; the squares are the outlines of the wire loop used for transmitting and receiving the transient electromagnetic signals (Raab and Frischknecht, 1985). As necessary, loops were laid out in an irregular pattern to avoid placing them directly over the numerous pipelines that exist in this field.

The transient soundings were inverted by using a layered-earth model. Using such a model causes the interpreted results (fig. 19.3) to be somewhat in error locally where there are rapid lateral changes in the resistivity of the section. Nevertheless, a useful picture of variations in electrical resistivity can be obtained from this approach. Away from the polluted area, the field data were closely fit by a four-layer model. In the vicinity of known surface brine contamination, interpreted resistivities were generally lower, and the layering was disrupted, as shown in figure 19.3. It is interesting to note that the resistivity of the upper layer has not been altered by the substantial brine seepage at the surface.

Water samples taken from test drill hole No. 2 (fig. 19.2) showed considerably higher salinities than those taken from Nos. 1 and 3 (Fitterman and others, 1986). Also, resistivities, as measured by induction logs, were lower in hole No. 1 than in holes No. 2 and 3, but they were not as low as expected from the surface soundings. Reasons for this discrepancy are not completely understood.

In this example, surface electromagnetic soundings clearly outlined a zone of extreme brine pollution. Undoubt-

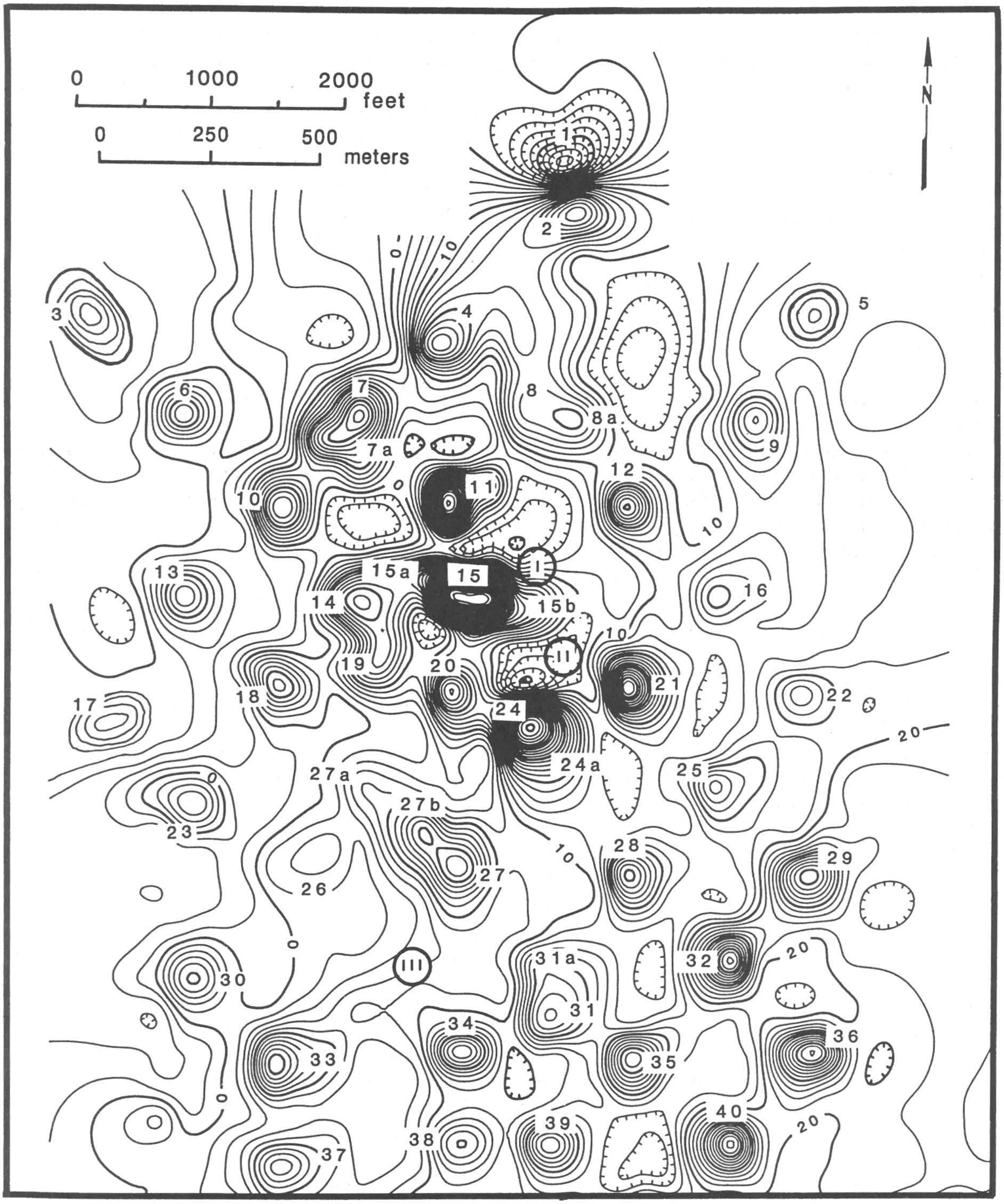
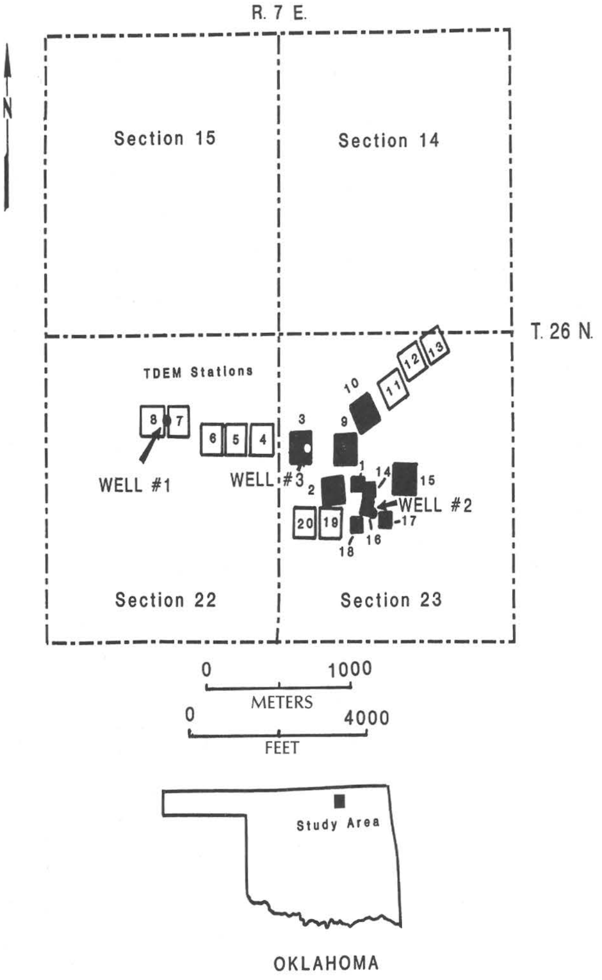


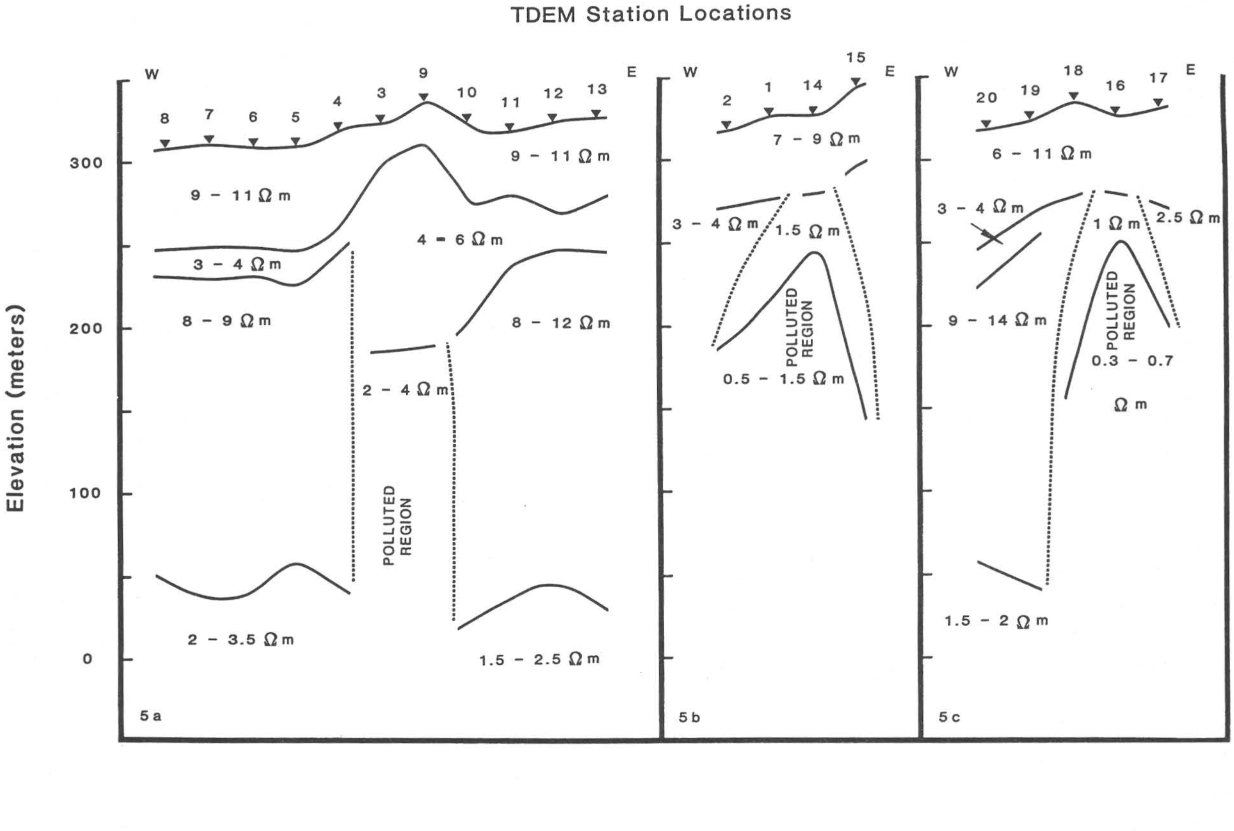
Figure 19.1. Aeromagnetic contour map over part of the Coon Creek oil field northeast of Oklahoma City, Okla. Flight altitude was 61 m above terrain, line spacing was 100 m, and contour interval is 2 nannoteslas. Magnetic features discussed in text are labeled with Arabic numerals. Photographically identified holes not reflected in contour map are labeled with Roman numerals.

edly, less intense pollution extends beyond the zone indicated in figure 19.3, but it cannot be detected because the resistivity of the unpolluted rocks in this area is very low. However, relatively low concentrations of brine or other electrolytes can be detected and mapped in rocks that have higher resistivities.



◀ **Figure 19.2.** Location of electromagnetic soundings and test drill holes near Pawhuska, Okla. The squares are outlines of wire loops used for transmitting and receiving signals. Darkened squares overlie polluted regions. TDEM, time-domain electromagnetic method.

Figure 19.3. Electrical sections interpreted from electromagnetic soundings. Regions of most intense brine pollution are indicated. Station numbers refer to locations on figure 19.2. TDEM, time-domain electromagnetic method; Ωm, ohm-m.



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20. The Use of Spectroscopy in Environmental Geochemical Studies

By Roger N. Clark *and* Trude V.V. King

Most minerals show diagnostic absorption features in the reflected solar radiation part of the spectrum (0.3–2.5 (μm) and in the thermal infrared part of the spectrum (8–14 μm). These absorptions can be used to determine the mineralogy of the surface and, in a growing number of cases, the trace elements present in those minerals. Mineralogy can be determined over large areas by using a new generation of airborne or spacecraft instrumentation called mapping (or imaging) spectrometers that obtain spectral data for millions of points on the surface.

Spectroscopy may prove to be a valuable environmental geochemical tool. Recent advances in laboratory studies of minerals at high spectral resolution have shown many narrow absorptions and fine structures not previously observed. As the absorptions are sensitive to the cation site locations, small changes in mineral chemistry may change the band positions. For example, iron can be detected at the parts-per-million level in most silicate minerals. It has recently been shown that nickel can be detected at the parts-per-thousand level in olivine (King, 1986), and manganese can be detected at the parts-per-thousand level and iron at the parts per million level in dolomite (Gaffey, 1984). In calcite, it has been shown that copper can be detected at the parts-per-ten-thousand level (Gaffey, 1984). This aspect of spectroscopy may prove extremely valuable in monitoring the environment. In addition, recent high-resolution studies of the magnesium-rich serpentine mineral group (King, 1986) have shown that it is possible to spectrally distinguish the isochemical end members chrysotile, lizardite, and antigorite (fig. 20.1). Other data show that spectral differences exist between the members of a solid solution series such as in tremolite-actinolite (fig. 20.2). In some cases, instead of different absorptions appearing with compositional or structural changes, small changes in band position appear, as illustrated with sodium or calcium montmorillonite (fig. 20.3).

In the last decade, remote-sensing instruments contained only a few spectral channels, but new medium-resolution spectroscopic instruments that have more than 100 spectral channels are already being flight tested. These new instruments can resolve fairly narrow absorption features and possibly detect subtle changes in band width. The identification of absorption bands means that direct identification and mapping of mineral type can now be accomplished. The near-infrared spectral region is very sensitive to OH-bearing minerals, especially clays. Detection levels of clays can be better than 1 percent, depending on data quality. This new generation of remote sensing instruments has the potential for mapping mineral type and potentially toxic contaminants in minerals at the surface over large areas. Similarly, handheld spectrometers can be used in the field to perform the same identifications on hand samples from the surface, a borehole, or bottom sediments.

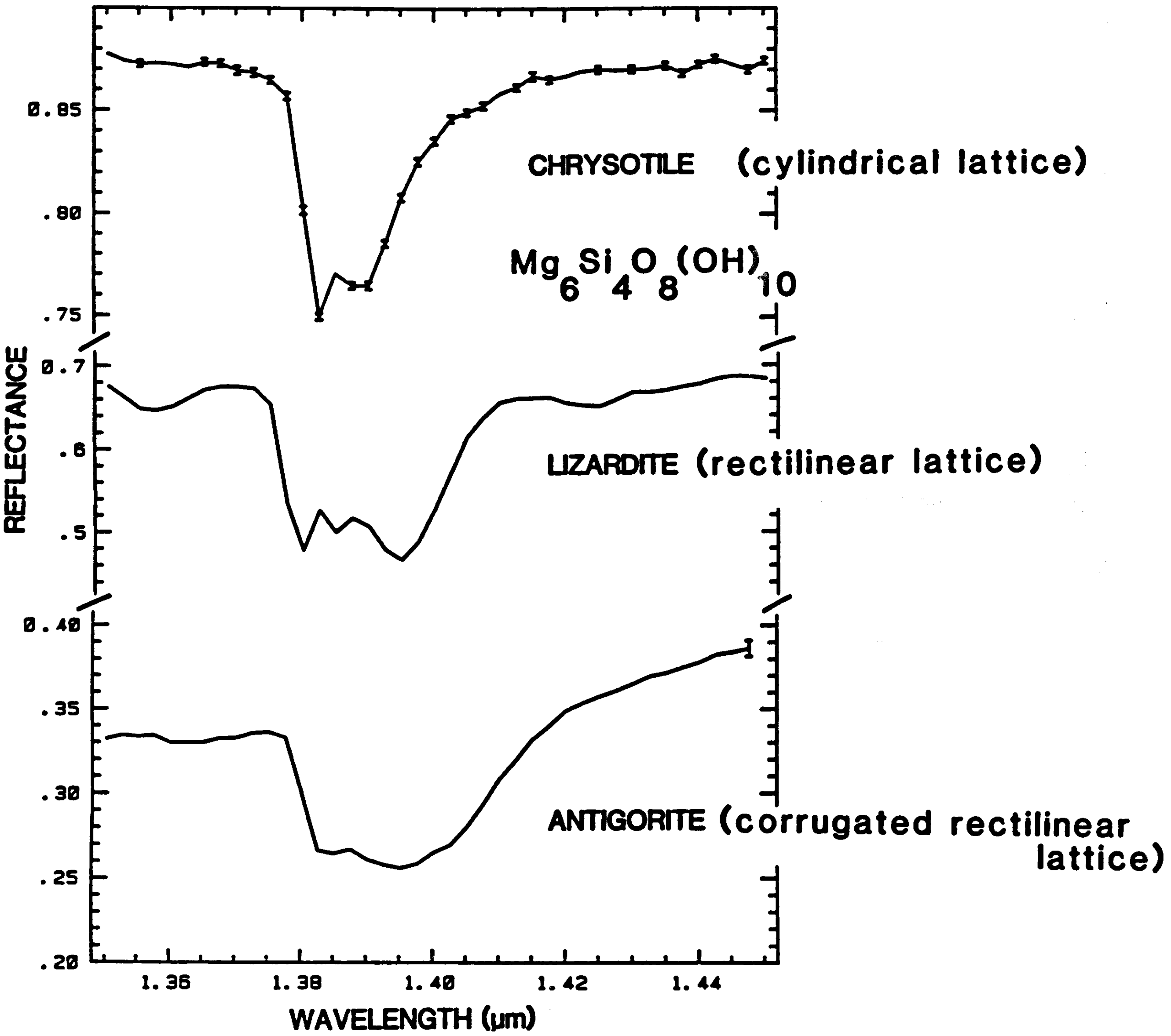

Figure 20.1. Near-infrared reflectance spectra of powdered chrysotile, lizardite, and antigorite. All three minerals have the same composition but different lattice structure. The small differences in structure cause slight differences in bond strengths of the OH radical and give different band positions and strengths. Spectra are at × 2 resolution.

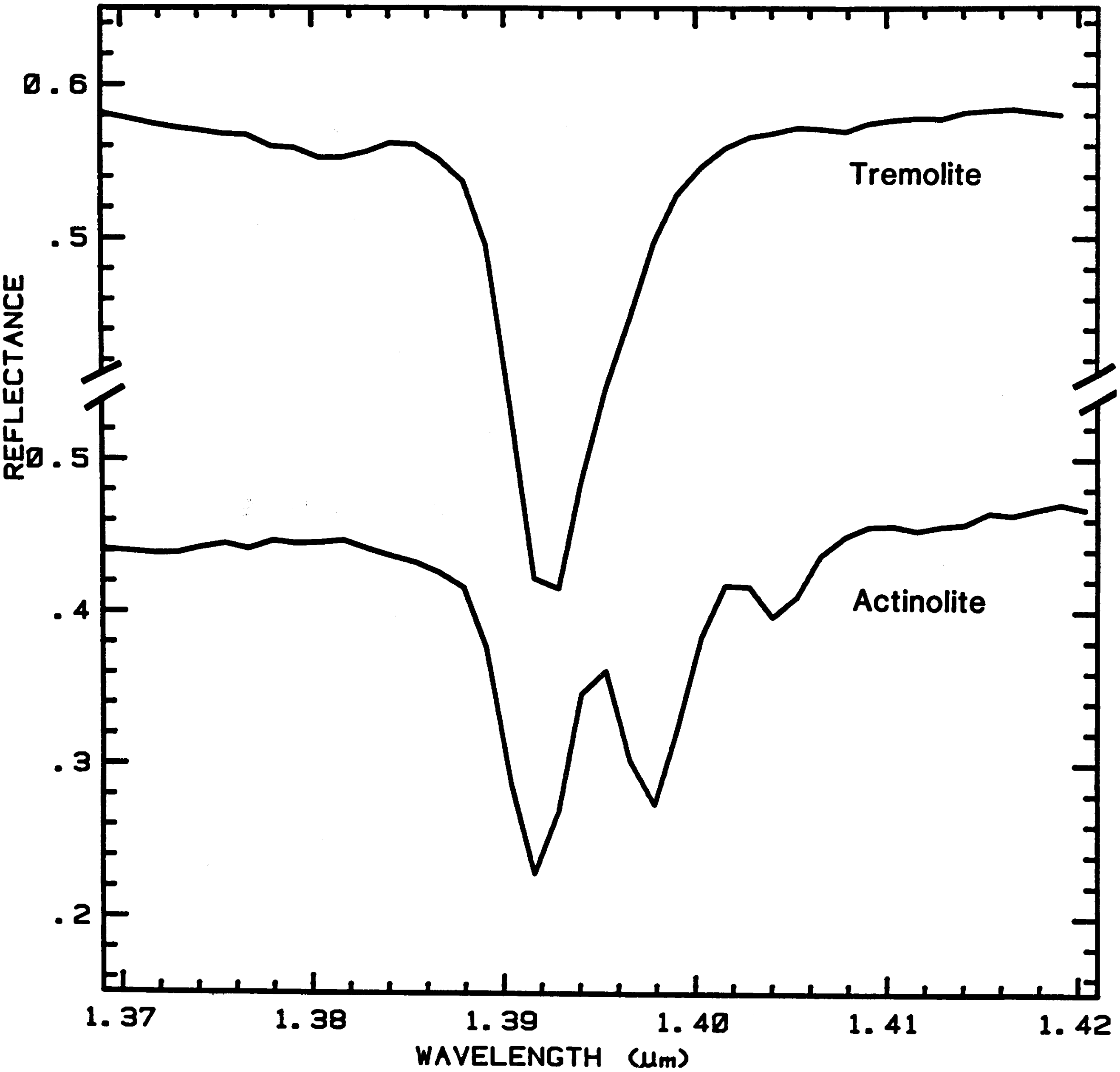

Figure 20.2. Near-infrared reflectance spectra of powdered tremolite and actinolite (composition $Ca_2(Mg,Fe^{+2})_5Si_8O_{22}(OH)_2$). The change in composition of this solid-solution series results in changes in the absorption bands.

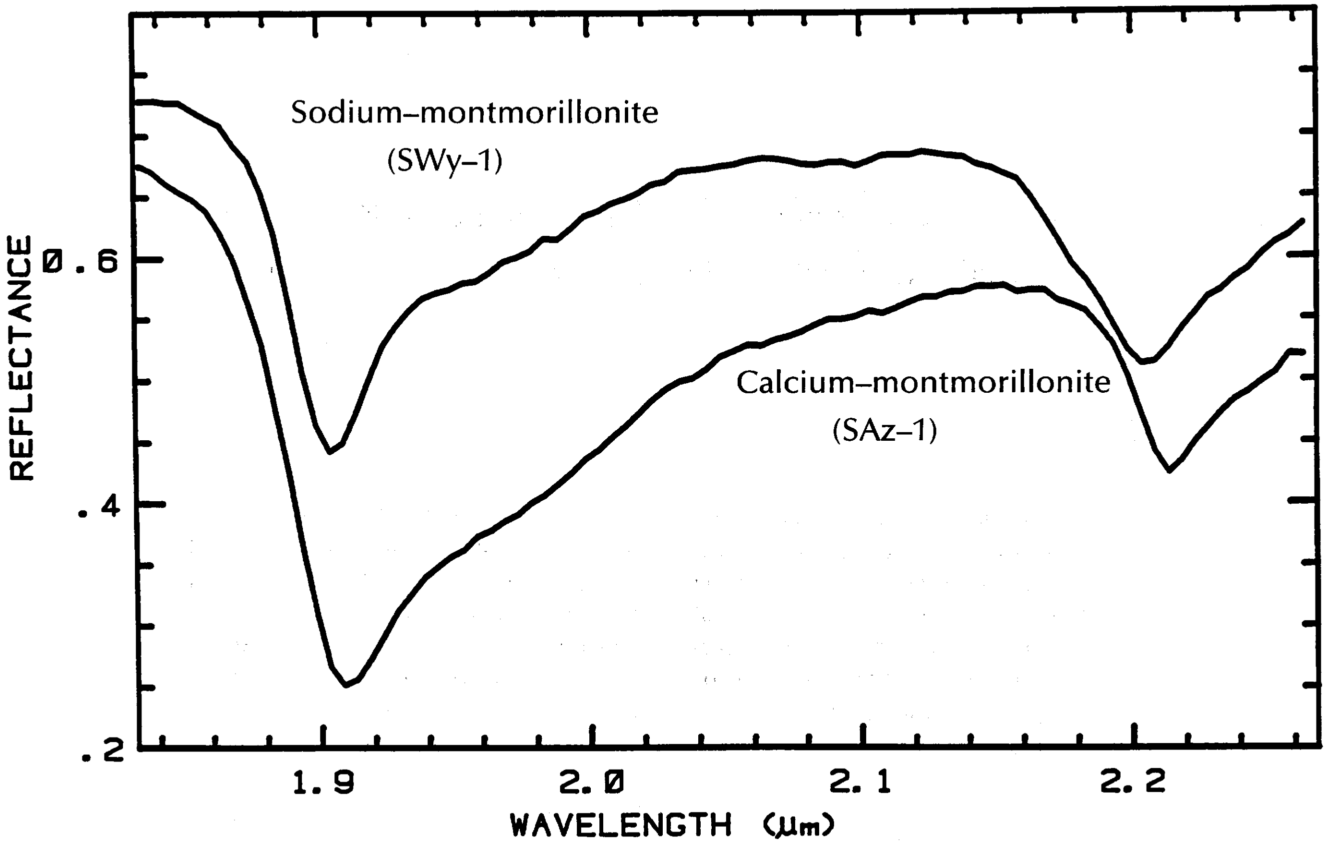

Figure 20.3. Near-infrared spectra of a sodium montmorillonite (SWy-1) and calcium montmorillonite (SAz-1). Note the small shift in the absorption band position near 2.2 µm. The CaO and Na_2O contents are 1.68 percent and 1.53 percent, respectively, for SWy-1, and 2.82 percent and 0.063 percent, respectively, for SAz-1.

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21. Application of Stable-Isotope Techniques to Environmental Geochemistry

By Elliott C. Spiker

SUMMARY

Stable-isotope techniques have been successfully applied to a wide variety of environmental and geochemical problems. Natural processes have established recognizable patterns in the distribution of the stable isotopes of several light elements. Knowledge of these patterns and an understanding of how natural processes affect the isotopic distributions help to determine the sources and histories of these elements in many geologic systems.

INTRODUCTION

Most environmental isotope studies have focused on the stable isotopes of hydrogen (^{1}H, ^{2}H), carbon (^{12}C, ^{13}C), nitrogen (^{14}N, ^{15}N), oxygen (^{16}O, ^{18}O), and sulfur (^{32}S, ^{34}S). These elements are involved in most geochemical reactions and are the important elements in biological systems. Human activities, such as the application of agricultural fertilizers, the combustion of fossil fuels, and the disposal of organic wastes, are often accompanied by measurable isotopic changes in the affected environments. Stable-isotope techniques can be used to trace both the precursors and products of reactions. Although in complex situations the results can be ambiguous, stable isotopes can serve the important function of testing and eliminating hypotheses of geochemical reactions. Because many natural sources have variable isotopic compositions, the emphasis of most stable-isotope studies is on isotopic variations and comparisons within well-defined systems. Comprehensive reviews of the many applications of stable-isotope techniques are given in Jäeger and Hunziker (1979), Fritz and Fontes (1980), and Hoefs (1980).

MINERAL AND WATER INTERACTIONS

Variations in the isotopic composition of meteoric water are primarily due to evaporation and condensation processes that are related to temperature, altitude, and latitude. Knowledge of the global patterns of the isotopic composition of hydrogen and oxygen in meteoric water can be used to determine the source and history of water, the mixing of ground water and surface water, and the location of ground-water recharge areas. Fractionation of stable carbon isotopes among gaseous, aqueous, and solid phases can be used in conjunction with mathematical models to determine the geochemical evolution of a ground water and to identify different sources of inorganic carbon in the water. The mass balance of carbon and carbon isotopes may be used to make corrections to measured ^{14}C ages of ground water. Also, the nitrogen isotopic composition of dissolved nitrate in surface and ground water can indicate the relative contributions of nitrogen from fertilizer and animal waste.

The isotopic patterns in waters often are reflected in the isotopic composition of certain sedimentary materials in isotopic equilibrium with the water, such as carbonate minerals, silica, clays, and evaporite minerals. The oxygen-isotope composition of these sedimentary minerals can be used to determine their formation temperature. The isotopic fractionations among water, CO_2, and carbonate minerals have been thoroughly studied because of the abundance of carbonate minerals in sedimentary environments.

Deep ground water may undergo oxygen-isotope exchange with aquifer rocks, particularly carbonate minerals, as depth and temperature increase. The resulting oxygen-isotope shifts in both the water and the rocks are then a useful indicator of this exchange process (for example, see Hearn and others, this volume). Such oxygen isotopic shifts may be large in hydrothermal systems. Stable carbon and oxygen-isotope compositions of carbonate minerals, in combination with an understanding of trace-element partitioning and textural changes during carbonate diagenesis, can provide information on the relative influences of meteoric or marine waters, sources of dissolved carbonate, changes in pore fluids, and the extent of rock and water interactions.

SOURCE AND DIAGENESIS OF SEDIMENTARY ORGANIC MATTER

Isotopic changes accompanying the decomposition of organic matter in anoxic sediments have been extensively studied. The microbial processes of sulfate reduction and methane production impart distinct isotopic signatures to the CO_2 and CH_4 produced. The isotopic composition of various authigenic carbonate minerals associated with organic-rich sediments may record isotopic changes resulting from geochemical evolution of the pore water.

The fate of pollutants adsorbed on particulate matter in aquatic systems is largely determined by the transport and deposition of these particulates. Stable carbon isotopes have been used in several studies as tracers of terrestrial organic matter in marginal marine environments (see reviews by Degens, 1969; and Deines, 1980). Carbon isotopes have also been used to estimate the contribution from estuarine algae to the organic matter in estuarine sediments (Spiker and Schemel, 1979; Spiker, 1981). Because of the complexity and variability of many of these systems, such studies require an understanding of the hydrology of the system and should be done in combination with other tracer techniques, such as elemental ratios (C:N) and lignin analysis (Hedges and Mann, 1979).

Environmental studies of sedimentary organic matter need to include a consideration of the effects of decomposition and formation of humic substances. Studies using carbon isotopes and solid-state nuclear magnetic resonance techniques (Hatcher and others, 1983; Spiker and Hatcher, 1984) indicate that the selective degradation of carbohydrates leads to a significant decrease in the $^{13}C/^{12}C$ ratio of the residual organic matter preserved in the sediment. These isotopic shifts are useful in the study of early diagenetic processes but must also be taken into account in isotopic tracer studies of sedimentary organic matter.

SOURCES AND EFFECTS OF ANTHROPOGENIC SULFUR

Assessment of man's contribution of sulfur compounds to the atmosphere is difficult because of natural variability; however, sulfur isotopes ($^{34}S/^{32}S$) promise to be very useful. Combustion of fossil fuels may produce sufficient sulfur oxides to significantly alter the isotopic composition of sulfur in sediments, soils, plants, and water. Studies of ^{34}S in rainfall have shown pronounced isotopic shifts in industrial areas (Krouse, 1980). Such effects are only beginning to be studied and offer great potential for environmental studies (for example, see Gough, this volume). Sulfur isotopes may prove useful in studies of acid rain and the role of atmospheric sulfur oxides in the dissolution of building stone. Our preliminary studies indicate that ^{34}S in the gypsum-rich crust that forms on the surface of exposed stone may distinguish atmospheric sulfur from sulfate that may be found naturally in the stone.

The formation of acid waters by the oxidation of pyrite-bearing ore deposits, mine tailings, and coal strata is a complex and serious environmental problem. These sources of sulfur may be distinguished isotopically from sulfate from evaporite minerals, the most common natural source of sulfate in surface waters. The sulfur and oxygen isotopic composition of sulfur compounds in surface waters can also give information on important biochemical transformations, such as the role of bacteria in pyrite oxidation (Taylor and others, 1984).

CONCLUSIONS

Stable-isotope techniques can be applied to a variety of environmental problems where they serve as tracers and as parameters for testing hypotheses of geochemical and biochemical reactions. These environmental studies benefit greatly from the large amount of information available concerning the geochemistry and global distribution patterns of the light elements and their isotopes. This information provides a context for the analysis of anthropogenic effects. Stable-isotope techniques are most successful when applied in conjunction with other techniques in a multidisciplinary fashion.

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22. Quaternary Geology and Pollution Problems—An Example from the San Francisco Bay Area, California

By Ed Helley

Geologic maps that emphasize engineering properties of surficial deposits provide much needed information pertaining to the areal distribution of sediment, including grain size, porosity, and permeability. These parameters govern the movement of ground water and are critical in predicting the probable migration rates and pathways of plumes of toxic waste. Mapping in urbanized terranes, however, poses several problems for the geologist, as most of the landscape is paved or graded and covered by urban sprawl. Specialized mapping techniques have been devised that enable the geologist to depict the geology in spite of the deleterious effects of urban development.

One such area, for example, that has not only undergone rapid growth but also has a severe pollution problem is the flatland region of south San Francisco Bay, a structural valley often referred to as Silicon Valley, the locus of a multibillion dollar electronic and semiconductor industry. Figures 22.1 and 22.2 illustrate the changing character of the valley floor from 1959 (chiefly orchards) to 1977 (chiefly urban). In 1986, the floor of the valley is even more densely urbanized.

A complex water supply system serves the south San Francisco Bay and its nearly 2 million residents. Water for municipal and industrial uses comes from ground water, impounded surface water, and surface water imported from the Sierra Nevada through San Francisco's Hetch Hetchy and South Bay Aqueducts. Ground water supplies more than half the region's drinking water. Therefore, avoiding contamination of the aquifers with toxic waste is vitally important. However, toxic wastes continue to threaten potable ground-water reservoirs. At present at least 100 contaminated sites are known in Silicon Valley. For example, in late 1981, a leak was discovered in underground storage tanks located at Fairchild Camera and Instrument Company in southern San Jose. The inventory and disposal records revealed that 60,000 gallons of solvent (trichloroethane or TCE) had been lost over an 18-month period. Some municipal wells situated down the hydraulic gradient were found to contain as much as 8,800 parts per billion (ppb) TCE (California Department of Health Services, 1984).

The U.S. Geological Survey is eminently qualified to provide information of pathways of toxic wastes in Silicon Valley. Helley and others (1979) mapped the geology of the flatlands of the bay region by using several innovative and specialized mapping techniques. The alluvial units were defined by geologic criteria, including depositional environment, geomorphic expression, soil-profile development, age, induration, compaction, and grain-size distribution. The distribution of geologic map units was determined from documents that predate urban development, such as topographic maps, soil maps published by the U.S. Department of Agriculture, and aerial photographs. Although soil maps were used to help construct the geologic map, the geologic map describes greater thicknesses than the uppermost 5 to 6 feet, an extrapolation largely based on the process by which the deposit was laid down. The depositional processes are influenced by active tectonism, climate change, and changing sea level caused by melting of continental glaciers.

Sometimes very old topographic maps, in this case one from 1895, can aid in differentiating pristine topographic features. For example, flood basins can be distinguished from alluvial fans or levees or tidal marshes. Figures 22.3, 22.4, 22.5, and 22.6 illustrate for a small area near Palo Alto, Calif., the kinds of maps used in compilations of an environmental geologic map for the San Francisco Bay region (Helley and others, 1979).

On the basis of relative soil-profile development, 18 alluvial soil series that were described by the Soil Conservation Service (1968) (fig. 22.4) were grouped by Helley and others (1979) into two distinct groups that reflect fundamental differences in the deposits in which they are developed. The soil units that have strongly developed weathering profiles constitute one group, and those that have weakly developed weathering profiles constitute another. The alluvial deposits characterized by strongly developed weathering profiles are inferred to be significantly

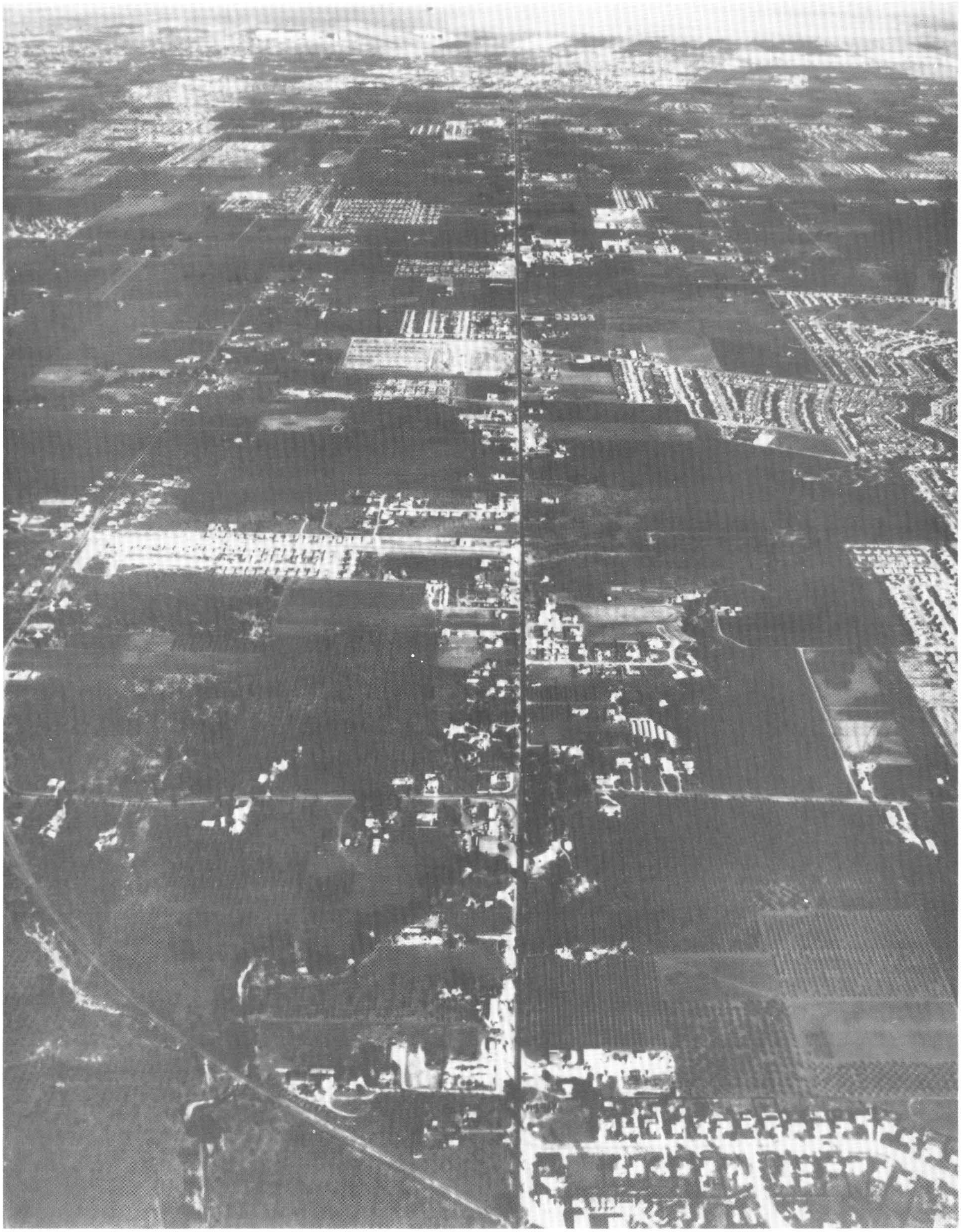

Figure 22.1. Aerial photograph of Silicon Valley, Calif., taken in 1959. Note agricultural character of the valley.

Figure 22.2. Aerial photograph of Silicon Valley, Calif., taken in 1977. Note urban character of the valley.

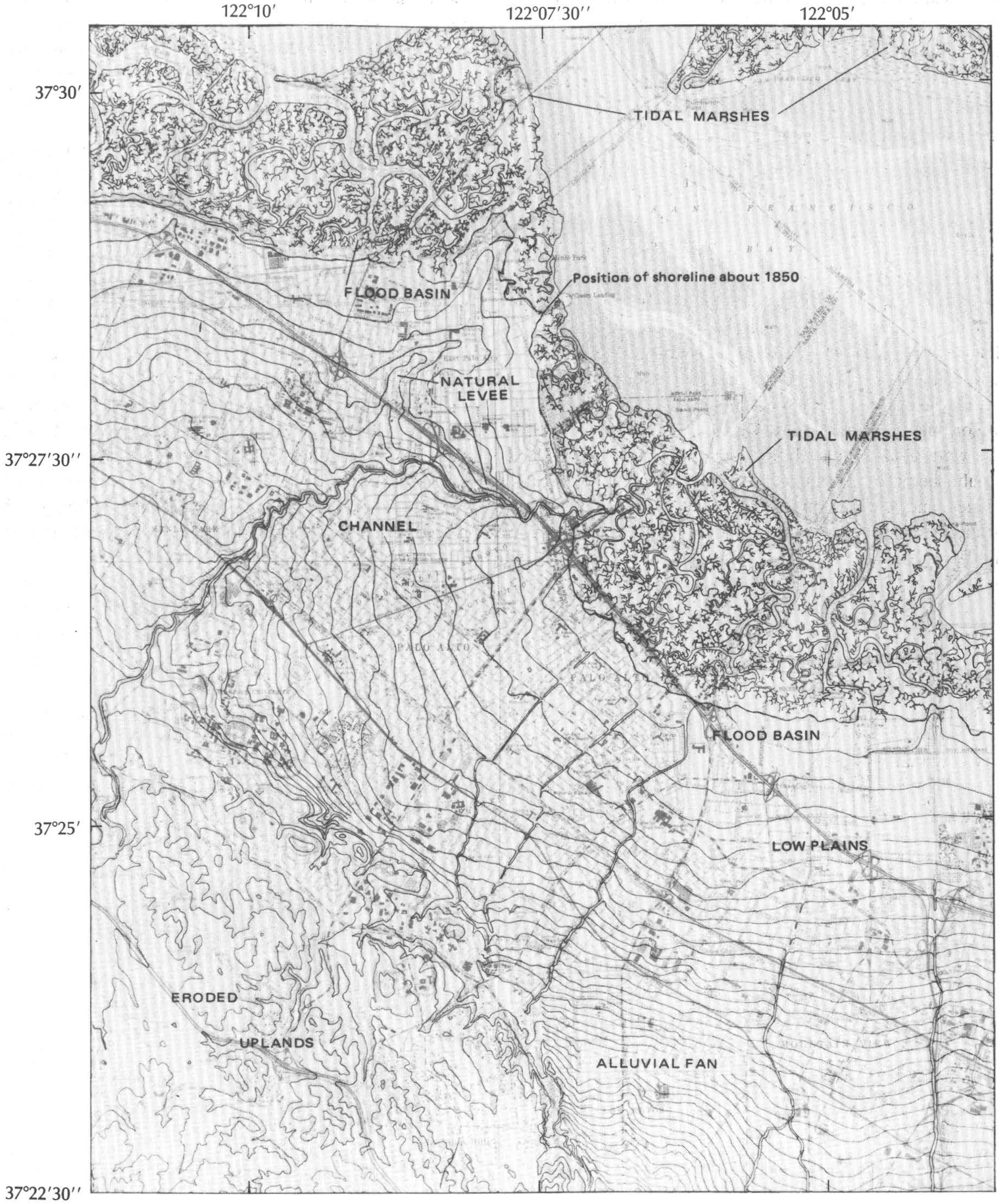

Figure 22.3. Alluvial deposits related to geologic processes in the Palo Alto area, California. The enhanced contour lines reveal the fluvial geomorphic features, alluvial fans, natural stream levees, and flood basins on the broad alluvial plain between the bay marshlands and the irregular bedrock uplands. Distribution of former tidal marshland from Nichols and Wright (1971). Base map from U.S. Geological Survey, Mountain View (1961, photorevisions as of 1973), Newark (1959, photorevisions as of 1973), Palo Alto (1961, photorevisions as of 1973), and Redwood Point (1959, photorevisions as of 1973) 1:24,000-scale quadrangles. From Helley and others (1979).

older than the deposits that have weak profiles. These two groups of deposits therefore simply indicate younger and older alluvial deposits.

The younger deposits constitute the alluvial fans formed under the present climatic regime. The present streams forming these younger fans are graded to present sea level. The older alluvial deposits now partly covered by the younger (Holocene) deposits make up alluvial fans formed by these same streams when they were graded to lower stands of sea level during the Wisconsinan glacial maxima about 18,000 years ago. At that time, sea level was lower by about 330 to 420 ft, and the Pacific shoreline was near the Farallon Islands some 36 mi west of the Golden Gate (Atwater and others, 1977). The Holocene alluvium is differentiated further into depositional facies on the basis of textural characteristics of surface soils; that is, the relative proportions of gravel, sand, silt, and clay. These textural data were obtained chiefly from published soil reports and unpublished engineering foundation reports for roads, bridges, and other structures. In addition, these deposits are differentiated by depositional environments (such as levees and flood basins) determined from geomorphic expression as shown on old topographic maps and aerial photographs. These stream deposits grade into and interfinger with fine-grained silt and clay deposits that form the flat floor of the alluvial flood basins between stream levees on the outer margins of the alluvial fans directly adjacent to the bay marshlands. The fine-grained basin deposits interfinger with and grade into the bay mud—the carbonaceous, wet silty clay that was deposited into the marshes and mudflats of San Francisco Bay as sea level rose as a result of the melting of glacial ice. The landward extent of the bay mud underlying former marshes and mudflats of San Francisco Bay was established from early (about 1850) U.S. Coast and Geodetic hydrographic charts (Nichols and Wright, 1971) rather than from direct field observation, because human activity over the past 100 years has obscured its original distribution.

Fossils, archaeological remains, and radiometric ages of deposits corroborate the relative ages and correlations based on these limited geographic and soils data. The upper part of the Pleistocene alluvial unit contains a (Rancholabrean) fossil vertebrate fauna consisting mainly of extinct species—camel, horse, bison, mammoth, and ground sloth. However, the Holocene alluvial deposits contain a fossil fauna that has a completely modern aspect (deer and elk).

When the late Pleistocene alluvial-fan drainages were graded to rivers that, in turn, were graded to a lower sea level, drainage channels were cut into older Pleistocene deposits. During the Holocene transgression of San Francisco Bay, these older channel deposits were buried by the encroaching bay mud and by early Holocene alluvium. These fossil channels today serve as conduits through which ground water moves downslope; these channels are numerous and comprise stringer aquifers.

The surficial mapping techniques described here will allow mapping of urbanized terranes, help geologists to predict where toxic waste is likely to travel, and indicate what surface areas are especially vulnerable to rapid infiltration of toxic fluids.

The U.S. Geological Survey should have an active role in such work, as it has already produced surficial maps of large areas of our country. For example, Helley and Harwood (1985) have completed such a map of the entire Sacramento Valley in California.

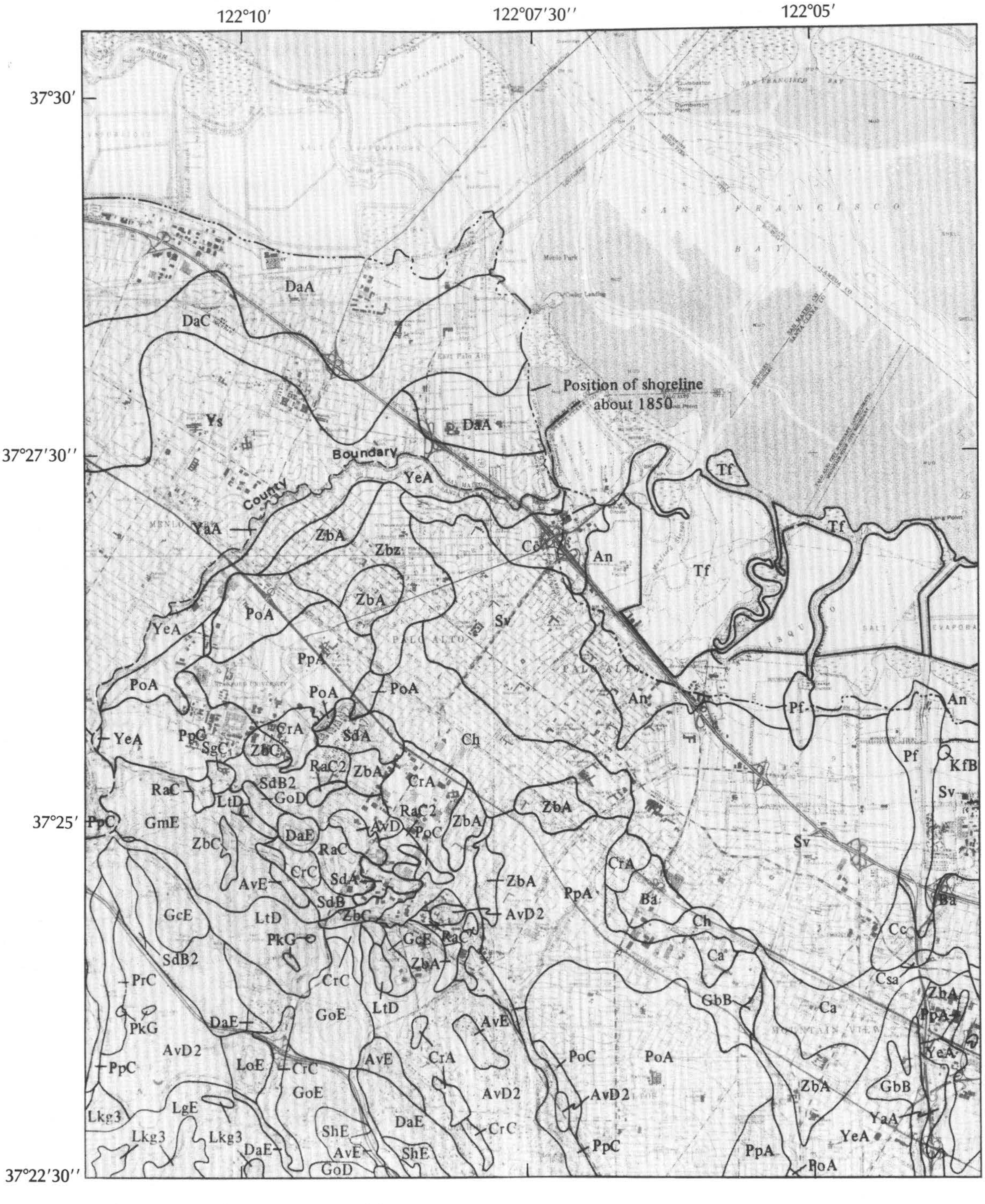

Figure 22.4. Soil units in Palo Alto area, California. Soil units are defined primarily on the basis of profile development, texture, and slope. Soil profile development is controlled by many factors including time, climate, parent material, slope, and biological activity. In this area where weathering conditions and parent material are relatively uniform, the time factor is clearly expressed by relative soil-profile development, which can therefore be used as a means of differentiating alluvial deposits on the basis of relative age. The symbols shown on the map refer to the names of local soil series (Soil Conservation Service, 1968). Base map from U.S. Geological Survey Mountain View (1961, photorevisions as of 1973), Newark (1959, photorevisions as of 1973), Palo Alto (1961, photorevisions as of 1973), and Redwood Point (1959, photorevisions as of 1973) 1:24,000-scale quadrangles. From Helley and others (1979).

EXPLANATION

Soil Series in the Palo Alto area*

Alluvial soil series with weakly to moderately developed weathering profiles:

An	Alviso clay
Ba	Bayshore clay
Ca	Campbell silty clay loam
Cc	Campbell silty clay loam, clay substrate
Ch	Clear Lake clay, drained
CrA	Cropley clay; 0- to 2-percent slopes
CrC	Cropley clay; 2- to 9-percent slopes
Csa	Cropley clay loam; 0- to 2-percent slopes
GbB	Garretson gravelly loam; 0- to 5-percent slopes
Pf	Pacheco loams, clay substrate
Sv	Sunnyvale silty clay, drained
YaA	Yolo loam; 0- to 2-percent slopes
YeA	Yolo silty clay loam; 0- to 2-percent slopes
Ys	Yolo loam; no slope given, taken from older survey
ZbA	Zamora silty clay loam; 1- to 3-percent slopes
ZbC	Zamora clay loam; 2- to 9-percent slopes
Zbz	Zamora clay loam; 0- to 2-percent slopes

Alluvial soil series with strongly developed weathering profiles:

PoA	Pleasanton loam; 0- to 2-percent slopes
PoC	Pleasanton clay loam; 0- to 2-percent slopes
PpA	Pleasanton gravelly loam; 0- to 2-percent slopes
PpC	Pleasanton gravelly clay loam; 2- to 9-percent slopes
RaC	Rincon clay loam; 0- to 2-percent slopes
RaC2	Rincon clay loam; 2- to 9-percent slopes
SdA	San Ysidro loam; 0- to 2-percent slopes
SdB	San Ysidro loam; 2- to 9-percent slopes
SdB2	San Ysidro loam; 2- to 9-percent slopes, eroded

Upland soil series (nonalluvial soils):

AvD	Azule silty clay laom; 2- to 9-percent slopes
AvD2	Azule silty clay loam; 9- to 15-percent slopes
AvE	Azule silty clay loam; 15- to 30-percent slopes
DaA	Diablo clay; 0- to 2-percent slopes
DaC	Diablo clay; 2- to 9-percent slopes
DaE	Diablo clay; 15- to 30-percent slopes
GcE	Gaviota loam; 15- to 30-percent slopes
GoD	Gilroy clay loam; 5- to 15-percent slopes
GoE	Gilroy clay loam; 15- to 30-percent slopes
GmE	Gaviota-Los Gatos complex; 15- to 30-percent slopes
LgF	Los Gatos clay loam
LoE	Los Osos clay loam; 15- to 30-percent slopes
Lkg3	Los Gatos and Maymen complex; 50- to 75-percent slopes
LtD	Los Trancos stony clay; 15- to 30-percent slopes
PrC	Positas-Saratoga loam; 2- to 9-percent slopes
ShE	Soper gravelly loam
SgC	Saratoga-Positas loam; 2- to 9-percent slopes

Miscellaneous map symbols:

KfB	Kitchen middens, archeological site
PkG	Gravel pits
Tf	Tidal mudflats

*From U.S. Soil Conservation Service (1968)

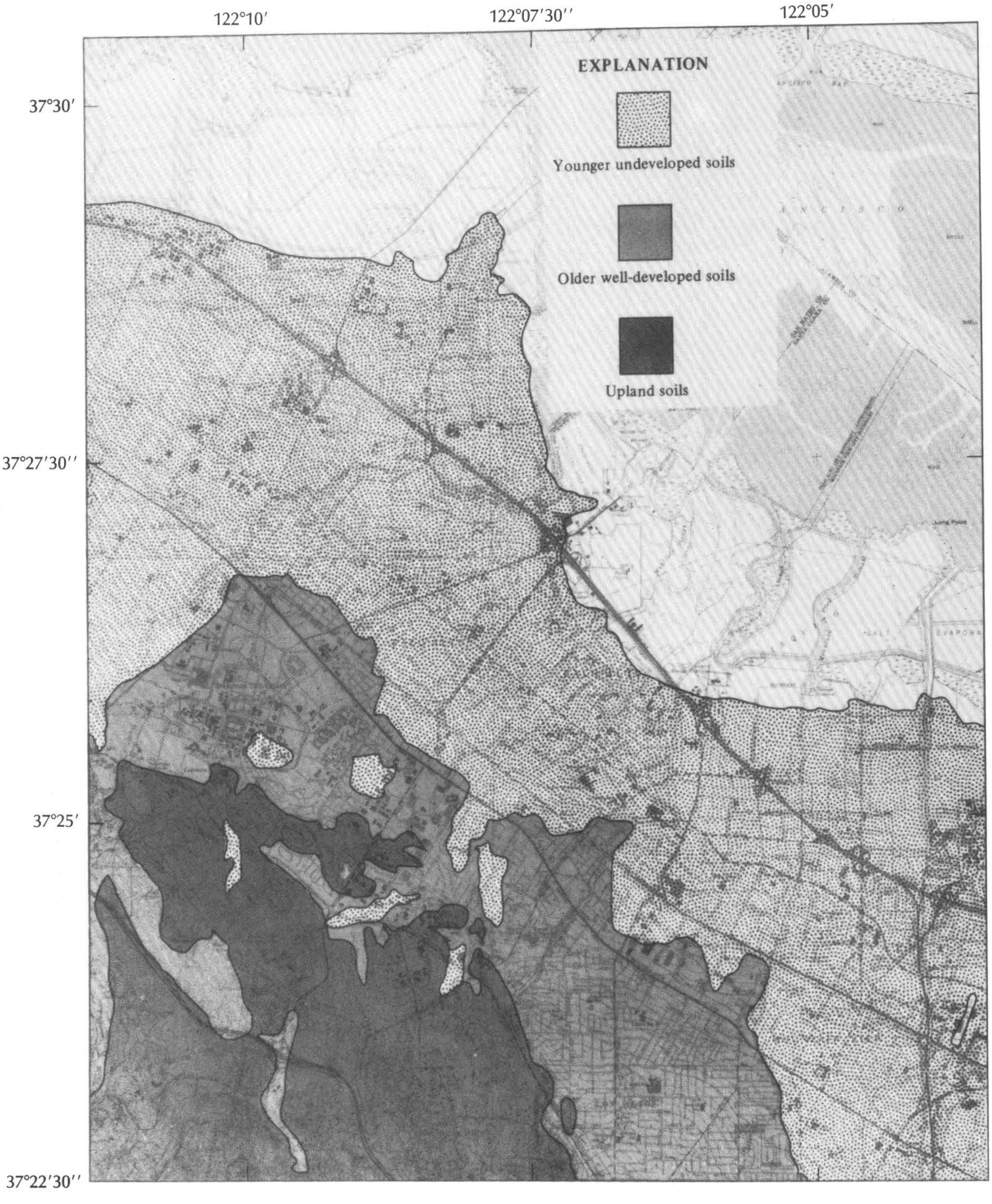

Figure 22.5. Distribution of younger and older alluvial deposits in the Palo Alto area, California, as determined primarily from relative soil-profile development of soil series as mapped by Soil Conservation Service (1968). Alluvial deposits on which weak to moderate weathering profiles are developed were initially inferred to be younger than alluvial deposits on which strong weathering profiles are developed. Radiocarbon and fossil data have confirmed this relative age classification. The younger alluvial deposits contain modern vertebrate and invertebrate fossils and organic remains that yield radiocarbon ages of about 5,000 years ago and younger. The older alluvial deposits locally contain extinct late Pleistocene vertebrate fossils, such as camel, sloth, bison, and mastodon, and organic remains that yield radiocarbon ages of about 20,000 years. Base map from U.S. Geological Survey Mountain View (1961, photorevisions as of 1973), Newark (1959, photorevisions as of 1973), Palo Alto (1961, photorevisions as of 1973), and Redwood Point (1959, photorevisions as of 1973) 1:24,000-scale quadrangles. From Helley and others (1979).

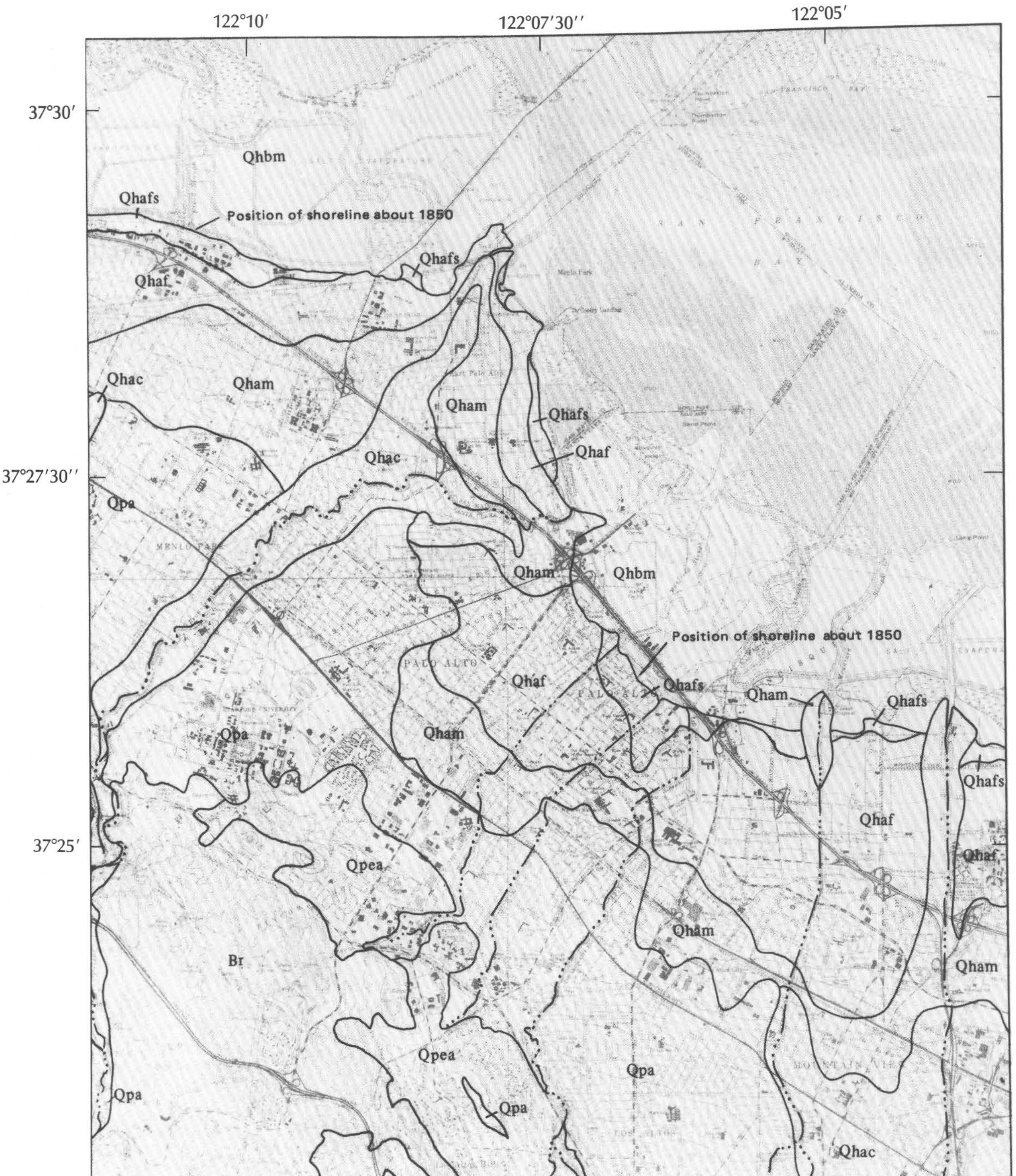

Figure 22.6. Surficial geologic map of the Palo Alto area, California. The symbols shown on the map refer to the names of local surficial and bedrock units. Dashed and dotted lines indicate drainages. Base map from U.S. Geological Survey Mountain View (1961, photorevisions as of 1973), Newark (1959, photorevisions as of 1973), Palo Alto (1961, photorevisions as of 1973), and Redwood Point (1959, photorevisions as of 1973) 1:24,000-scale quadrangles. From Helley and others (1979).

Description of Map Units

Holocene deposits (less than 10,000 years old):

Estuarine deposits (0-9,000 years old):

Qhbm Bay mud. Water-saturated estuarine mud; predominantly clay and silty clay underlying marshlands and tidal mudflats of San Francisco Bay. Contains a few lenses of well-sorted fine sand and silt and a few shelly and peaty layers. Interfingers with and grades into fine-grained and medium-grained alluvium; generally overlies early Holocene alluvium or late Pleistocene alluvium 0-120 ft (0-40 m) thick.

Alluvial deposits (0-5,000 years old):

Qhaf Fine-grained alluvium. Plastic, poorly sorted carbonaceous clay and silty clay in poorly drained interfluvial basins marginal to bay marshlands. Locally contains thin beds of well-sorted silt, sand, and fine gravel; contains modern vertebrate fossils and fresh-water gastropod and pelecypod shells. Interfingers with and grades into bay mud and medium-grained alluvium; overlies late Pleistocene alluvium. Generally less than 15 feet (5 m) thick.

Qhafs Salt affected fine-grained alluvium; same as Qhaf but containing high concentration of salt.

Qham Medium-grained alluvium. Loose, moderately drained, moderately sorted sand forming alluvial plains and stream levees. Locally contains beds of well-sorted clay, silt, and gravel; contains modern vertebrate fossils and fresh-water gastropod and pelecypod shells. Intermediate in character and lateral extent between fine-grained and coarse-grained alluvium with which it interfingers; generally overlies late Pleistocene alluvium. Generally less than 21 feet (7 m) thick.

Qhac Coarse-grained alluvium. Loose well-drained, moderately sorted, permeable sand and gravel forming stream levees and flood plains on higher parts of alluvial fans; gravel becomes dominant toward fan heads. Locally contains beds of well-sorted silt, sand, and gravel; contains modern vertebrate fossils and fresh-water pelecypod and gastropod shells. Thickness ranges from as much as 50 feet (15 m) at fan heads to 20 feet (6 m) where these deposits interfinger with and grade into medium-grained alluvium; overlies late Pleistocene alluvium and bedrock.

Pleistocene deposits (10,000-3,000,000 years old):

Qpa Late Pleistocene alluvium (10,000-70,000? years old). Weathered, slightly consolidated and indurated alluvial fan deposits consisting primarily of gravel and sand with some silt. Less permeable than Holocene alluvium. Locally contains fresh-water pelecypod and gastropod shells and extinct late Pleistocene vertebrate fossils. Overlain by Holocene deposits on lower parts of alluvial plain; incised by channels that are partly filled with Holocene alluvium on higher parts of alluvial plain. Maximum thickness unknown but at least 150 feet (45 m) near margins of present bay where these deposits overlie deeply buried Pleistocene estuarine deposits.

Bedrock:

Qpea Early Pleistocene and Pliocene alluvium. Tectonically deformed alluvial-fan deposits with local minor amounts of shallow-water marine deposits. Weakly to moderately indurated gravel, sand, and silt with subordinate amounts of lacustrine silt and clay; local thin tuff beds; contains late Pliocene and early Pleistocene vertebrate fossils. Underlies late Pleistocene alluvium; overlies or in fault contact with Franciscan Formation. Consists of the Santa Clara Formation in southwest bay area.

Br Undifferentiated Tertiary bedrock. Well-indurated sandstone, shale, and volcanic rocks. In map area underlies or is in fault contact with Pliocene and early Pleistocene alluvium.

Figure 22.6—Continued.

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23. Toward a Capability for Predicting Transport of Sediments on the Continental Shelf and Slope and in Submarine Canyons Along the Northeast Coast of the United States

By Bradford Butman

For the last 10 years, the U.S. Geological Survey, in cooperation with the U.S. Minerals Management Service, has made extensive observations of currents and sediment movement along the East Coast of the United States. Measurements using moored current meters and special bottom-mounted instrument systems (Butman and Folger, 1979; Strahle and Butman, 1985) were made on the continental shelf from 1975 to 1982 (fig. 23.1*A*); in Lydonia and Oceanographer Canyons from 1980 to 1982 (fig. 23.1*B*); and on the outer shelf and upper slope from 1982 to 1984 (fig. 23.1*C*). The long-range objective of this ongoing research is to provide a regional description of the

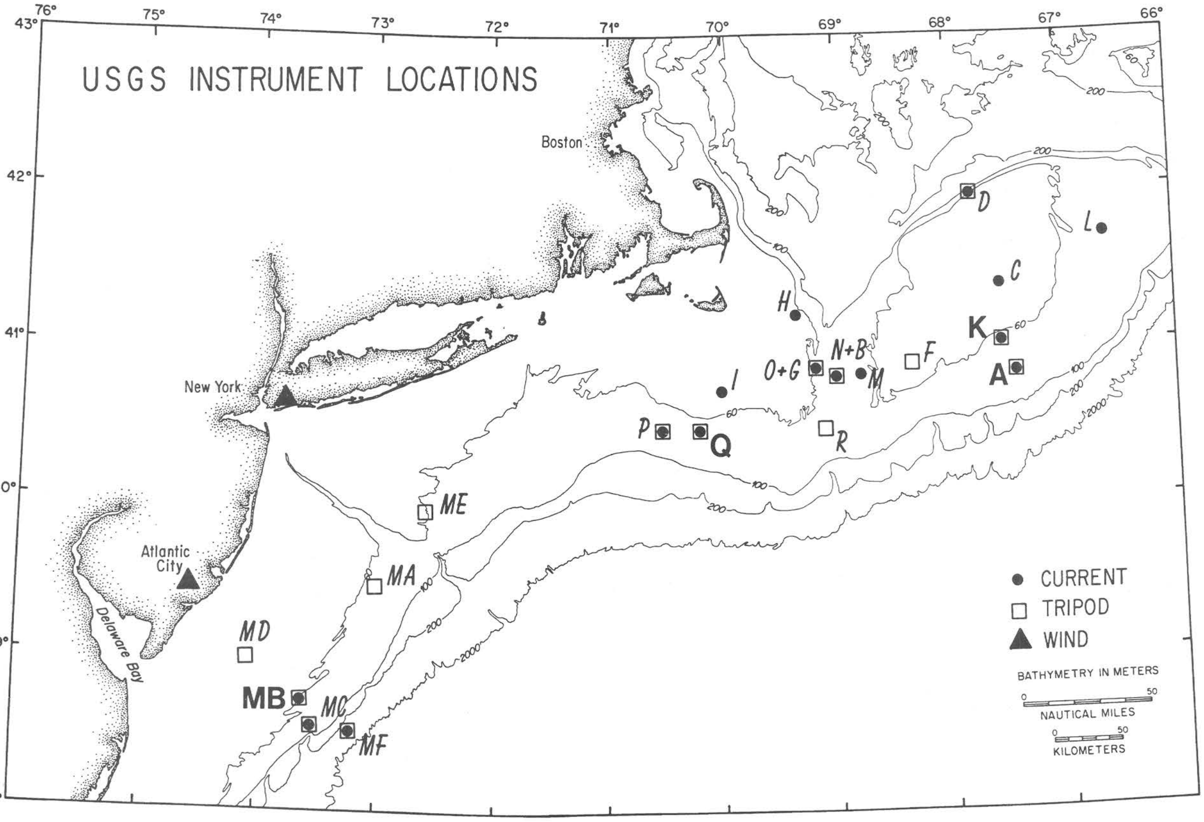

Figure 23.1. *A*, Location of instruments deployed on the continental shelf between 1975 and 1982. Stations A, K, Q, and MB were maintained as long-term stations (for 2 to 4 years), while the other stations were occupied for 1 to 6 months as part of shorter term experiments. Base map modified from Uchupi (1968).

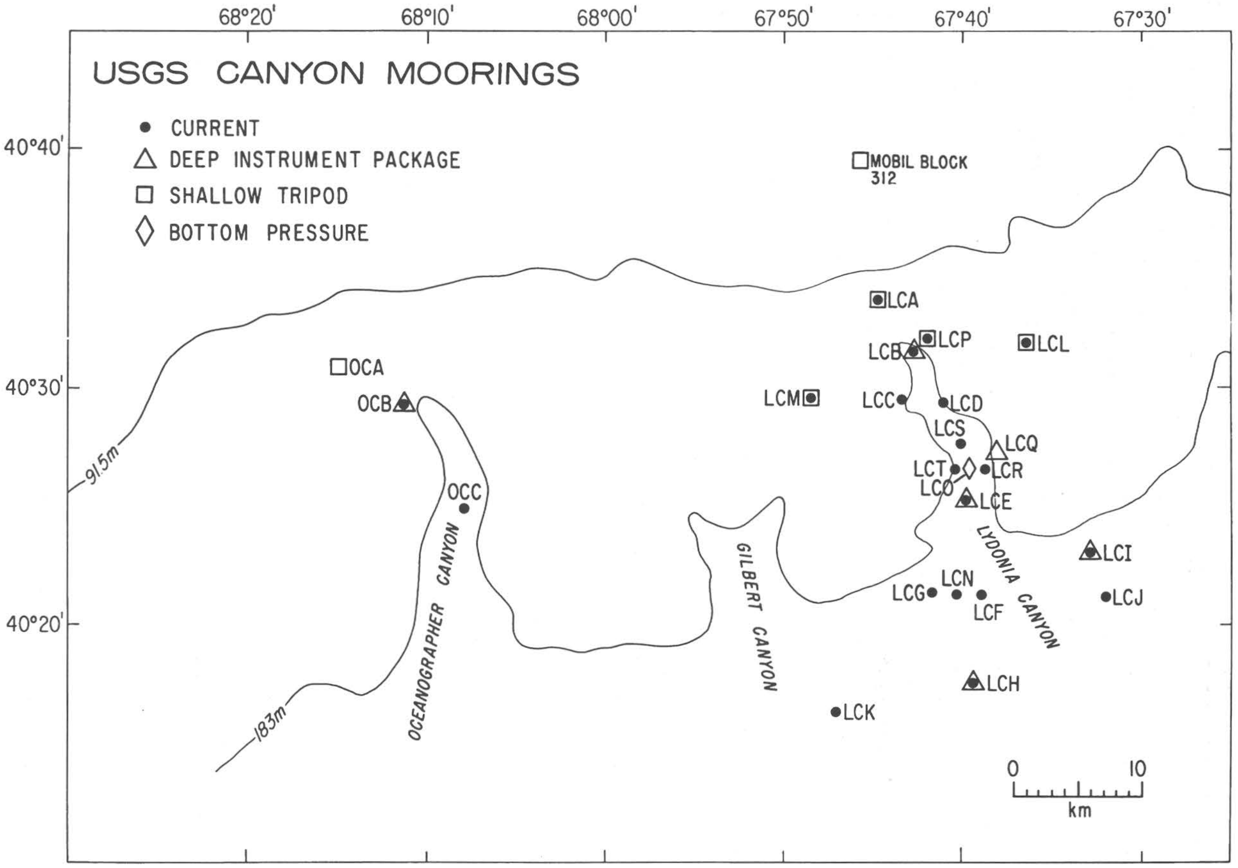

Figure 23.1. *B*, Location of instruments deployed in and around Lydonia and Oceanographer Canyons as part of the Canyon Dynamics Experiment conducted from 1980 to 1982. Stations LCA, LCB, and LCI were maintained as long-term stations, while the other stations were occupied for 1 to 6 months as part of shorter term experiments. Bathymetry from National Ocean Survey Charts 13203 and 13204.

physical oceanography and associated sediment movement. Knowledge of where and how fast sediment is transported can be used to plan monitoring studies, to evaluate possible environmental consequences of man's activity on the Outer Continental Shelf, and to understand the present distribution of surface sediments. Of special interest are the transport and ultimate fate of fine-grained sediments, to which man-induced pollutants readily adhere, and of drill muds and cuttings.

The present focus of this program is the analysis and synthesis of the large data set. Analysis of the measurements made in the canyons and on the slope is expected to continue through 1989. Papers describing the mean circulation on Georges Bank (Butman and others, 1982, 1983; Butman and Beardsley, 1987; Butman and others, 1987); sediment transport in the Middle Atlantic Bight (Butman and others, 1979) and on Georges Bank (Bothner and others, 1981; Twichell and others, 1981, 1987; Butman and Moody, 1983; Twichell, 1983a; Butman, 1987); and the low-frequency currents (Noble and others, 1983, 1985), the tidal currents (Moody and others, 1984), and the geology and bathymetry of Lydonia Canyon (Twichell, 1983b; Butman and Moody, 1984) have been published. These analyses provide a description of the physical oceanography of the region, which is essential background for regional studies of sediment transport.

The observations show that sediment movement of varying intensity is caused by several processes that affect different regions of the continental margin for various lengths of time. Over long periods of time, these intermittent transport events determine the distribution of sediments on the sea floor. On the crest of Georges Bank, the strong tidal currents cause nearly continuous sediment movement and, in concert with the westward residual flow, cause a net westward transport of fine-grained sediment along the south flank of Georges Bank toward the Middle Atlantic Bight. An area of fine-grained sediment on the shelf south of Cape Cod is a major modern sediment deposit along this transport pathway (fig. 23.2). Storms, particularly in winter, cause intense transport of fine-grained material back and forth

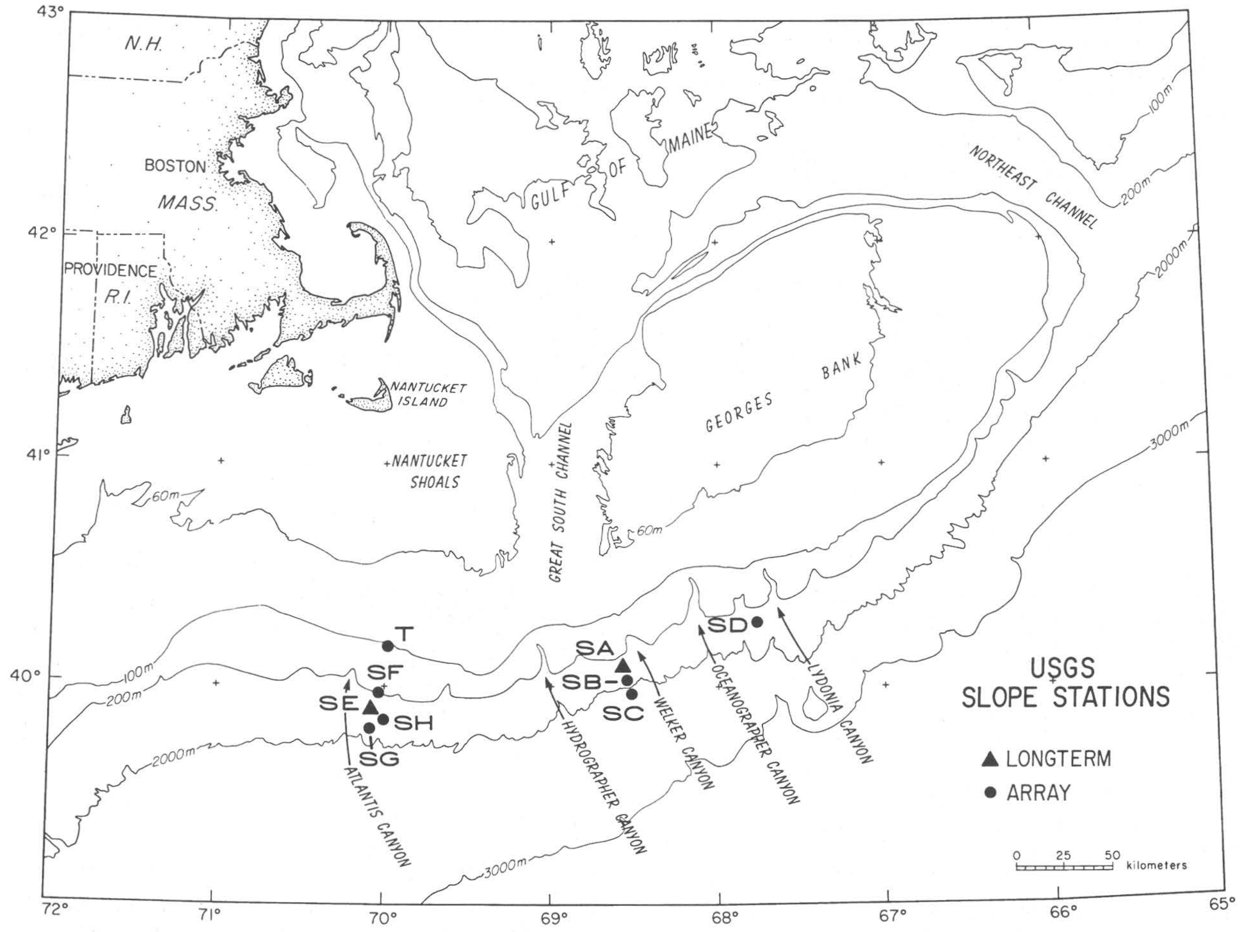

Figure 23.1. *C*, Location of instruments deployed on the outer shelf and slope between 1982 and 1984 as part of the Slope Experiment. Stations SA and SE were maintained as long-term stations. Base map modified from Uchupi (1968).

along the shelf, primarily parallel to the shelf edge. On the crest of Georges Bank, this episodic movement by storms is in addition to the nearly continuous movement by the tidal currents. However, over the rest of the bank in water deeper than about 60 m and on the shelf in water depths less than about 100 m, storms are the most important cause of sediment resuspension. During storms, the oscillatory currents associated with surface waves are principally responsible for increasing the bottom stress above the level required for movement to occur, whereas net transport is caused by the quasi-steady wind-driven flows. Because the near-bottom currents caused by waves decrease rapidly with water depth, sediment resuspension by waves is more intense in shallower water. The relative rates of net sediment transport caused by storms and by the tidal current-mean flow process described above remains to be determined.

Analysis of the observations made on the slope and in the submarine canyons is not complete; thus only preliminary results are available (Butman, 1988a,b; Csanady and others, 1988). On the outer edge of the shelf, a slight mean near-bottom off-shelf flow, coupled with strong currents associated with internal waves and Gulf Stream warm-core rings, winnows sediments from the shelf break. In the large submarine canyons, strong currents apparently caused by internal tides cause intense sediment movement. The net direction of bedload transport along the axis of the canyons caused by these flows may be upcanyon or downcanyon, and the observations show that the strength of the flow varies from canyon to canyon. There is apparently little sediment movement caused by currents on the continental slope in water deeper than about 300 m.

These observations made in different physiographic regions of the margin provide a framework for assessing the extent and direction of modern sediment transport on a regional basis and for predicting the ultimate fate of material introduced onto the margin. Because the oceanographic processes that transport sediments vary throughout the Georges Bank region, the fate of material will depend on its physical characteristics (size and density) and on

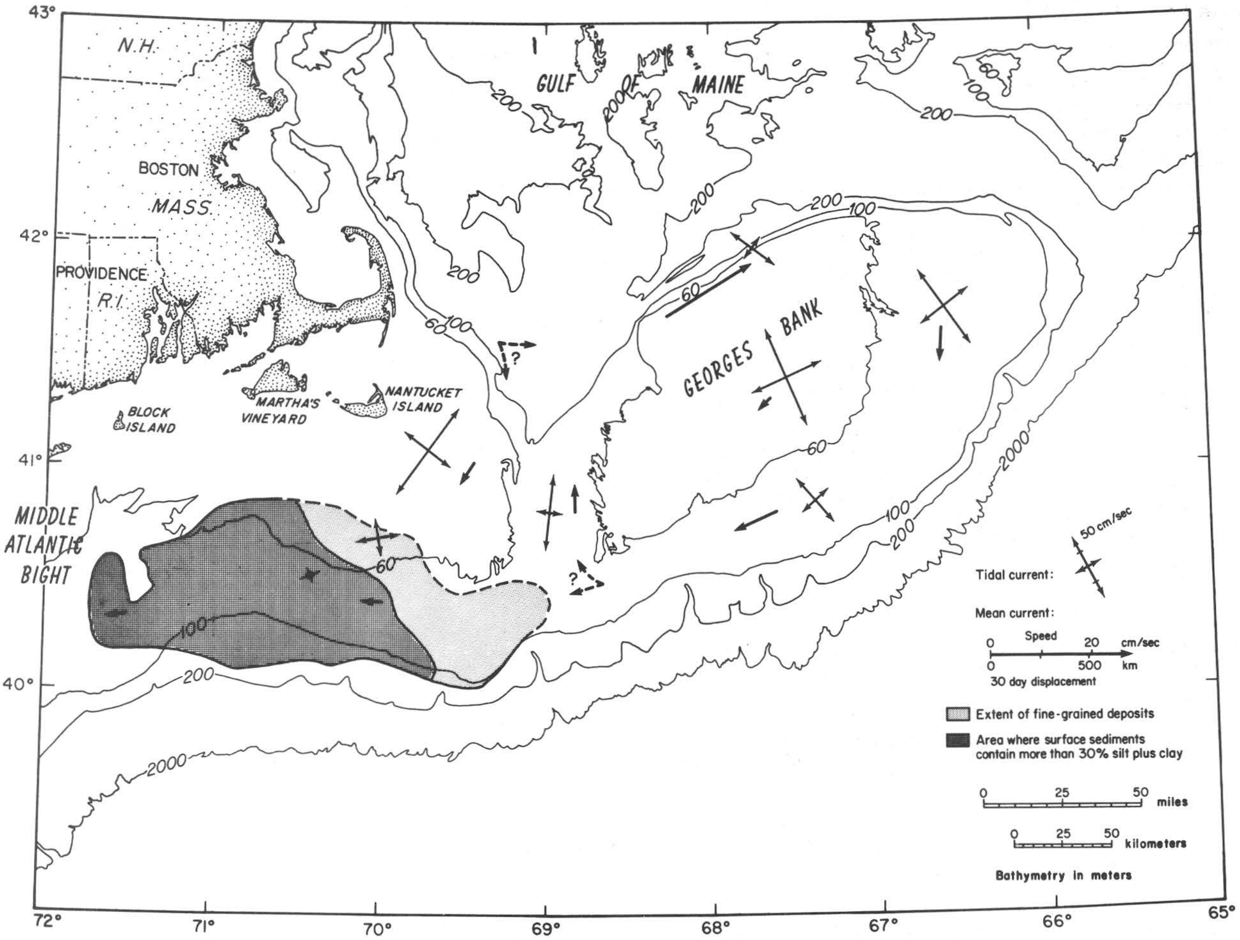

Figure 23.2. Summary diagram of tidal currents (two-headed crossed arrows represent the tidal ellipse) and mean currents (bold arrows) on Georges Bank, Nantucket Shoals, and the southern New England shelf. Shaded area is the location of the fine-grained sediment deposit; note the decrease in the strength of the tidal currents over this deposit. From Twichell and others (1981).

where the material is introduced. The observations suggest rapid dispersal of fine sediment (silts and clays) introduced onto the crest of Georges Bank and dispersal and westward transport of fine sediment introduced onto the south flank. Bedload transport of coarser sand-sized sediments is probably also slightly westward and offbank. On the open slope in water deeper than 300 m, sediments that reach the sea floor will probably remain for long periods of time.

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24. Characteristics of Coal-Mine Wastes for Rehabilitation Work

By R.C. Severson

Many of the soil-element availability techniques commonly used in agronomy are being applied to mine-rehabilitation sites because of the need for monitoring metal levels in both plants and mine soils. This application was prompted by mandates from reclamation guidelines. In actuality, these tests have proven to be most reliable for establishing deficiency levels of trace elements in soils. Using the same tests to define toxicity or maximum permissible levels (MPL) has caused much confusion for both regulators and mine operators. Plant species used in mined-land rehabilitation probably do not respond the same as agricultural plants in their uptake or exclusion of trace elements. Because recommendations differ for each agricultural crop, similar allowances should be made for each rehabilitation species. If doubts exist concerning the stated permissible levels and how they should be determined, then inequitable enforcement of regulations may result when enforcement is based on interpretations of these soil tests for different rehabilitation plant species.

To test the usefulness of diethylenetriamine pentaacetic acid (DTPA) a predictor of soil-plant relations, we sampled 11 areas (fig. 24.1) that varied greatly in edaphic, geological, geochemical, and climatic conditions and in mining and rehabilitation practices.

In the Western United States, DTPA-extractable metal levels in soil and overburden have been used as indicators of potentially toxic conditions for plant establishment and growth on rehabilitated land. Proposed upper limits, or permissible levels, and actual concentrations in both natural soils and mine soils in the northern Great Plains are given in Severson and Gough (1981, 1983). These studies indicate that DTPA-extraction measures under field conditions are inadequate for relating available metals in mine soils to metal uptake by rehabilitation plant species. Extraction measures do, however, provide data useful in defining provisional plant-physiological-tolerance ranges, while further basic research is conducted on the mine soil-plant system.

Proposed MPL's of trace elements were compared to the measured DTPA-extractable concentrations in cover soil, spoil, and A and C horizons of natural soil. In all these materials, the maximum levels of copper, manganese, lead, and zinc were well below the proposed MPL. For cadmium and nickel, the maximum amounts measured in cover soil and spoil at several mines, as well as 95 percent in A and C horizons of native soil, exceeded the proposed MPL. At only one mine was iron in spoil greater than the proposed MPL, but iron in cover soil and spoil at several mines was greater than that expected in natural soils.

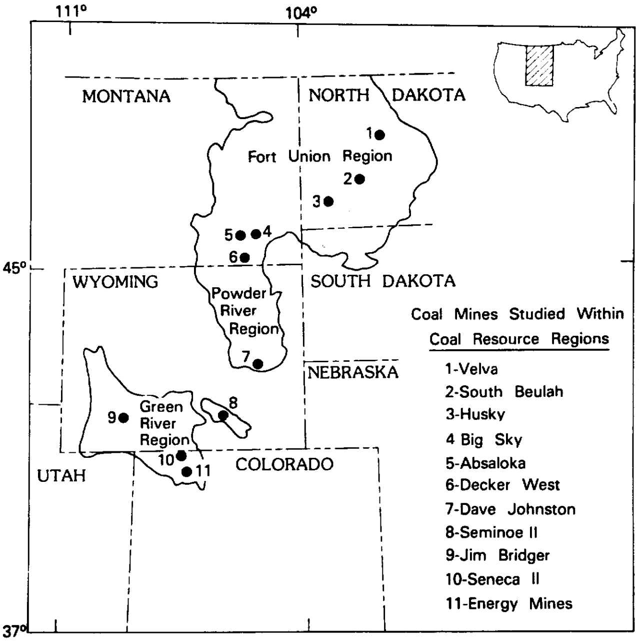

Figure 24.1 General locations of the coal surface mines sampled in the Western United States. From Severson and Gough (1984.)

Mine soils represent a youthful stage of soil development, and the rapid changes in their chemical equilibrium should be expected. The sedimentary rocks that were previously confined to a presumed reducing and biologically inactive zone are exposed by mining to an oxidizing environment that is biologically active.

Many soil extractants have been proposed as being universal for both native and disturbed soils but were subsequently abandoned. The concepts of intensity and capacity factors may be good starting points for the development of soil extracts for use on overburden material and soils of rehabilitated strip mines. How these factors might be applied to the development of new soil extracts is summarized here from a written communication by G. Sposito (University of California-Riverside, 1982). Potential bioavailability (capacity factor) of trace elements in rehabilitated mine soils can be estimated from extracts by using chelates such as ethylenediaminetetraacetic acid (EDTA) or DTPA only after the action of these chelates on minerals has been established. In general, chelate extractability implies susceptibility to weathering over time, whereas inorganic acid extractability implies resistance to weathering over time. Actual bioavailability (intensity factor) of trace elements in rehabilitated mine soil can be estimated from a water-saturation extract. This estimate might best be done by leaching mine soils with natural water (for example, precipitation) and determining the solubility of the solid phase of the soil during the leaching process. Such data would be useful in describing the actual bioavailability over short time periods. In addition, the leachate composition would be used to assess trace-element mobility.

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25. The Role of Coal Characterization in the Control of Acid Precipitation

By Jack H. Medlin *and* Frederick O. Simon

INTRODUCTION

Recent studies by the Committee on Atmospheric Transport and Chemical Transformation in Acid Precipitation (1983) and the General Accounting Office (1981) have concluded that atmospheric acid precipitation constitutes a hazard to man's environment. They further suggest that emissions from coal-fired powerplants may contribute significant amounts of acid-causing elements to the atmosphere. Their conclusions indicate that much research is necessary before the legislative process forces changes in operating procedures that may be excessively costly or ineffective. There is much uncertainty among policymakers, scientists, economists, and executives as to how to mitigate the effects of acid rain and to control the amount of sulfur emitted from coal-fired powerplants. One recommended solution to the problem includes tightening the standards of the Clean-Air Act to reduce sulfur dioxide emissions, which would be accomplished by the installation of scrubbers on existing and future powerplants. This approach may be sound from scientific and engineering viewpoints, but for older powerplants, it may be unsound from an economic viewpoint. The ongoing debate in various trade, scientific, and technical publications leads one to conclude that there is wide disagreement on the approaches to the solution of the problem. We believe that the application of scientific and technical methods, heretofore not widely considered, may alleviate the need for intensive application of scrubber technology and may help to obviate the need for scrubbers in individual cases. Although these approaches have not been entirely overlooked, they have not been emphasized to the extent that we feel is necessary to contribute to solutions of the acid-precipitation problem and to help with the continued or expanded use of coal.

PAST AND CURRENT STUDIES

Before 1984, most studies emphasized environmental monitoring as a means of determining whether a problem existed. Atmospheric distribution was studied to delineate possible sources of acid rain and to track its geographic progress; physiochemical pathways were investigated to ascertain reaction mechanisms; and observations were made of the effect of acid precipitation on various biologic, hydrologic, and geologic systems (National Acid Precipitation Assessment Program, 1983). These approaches address only half of the system with which we are dealing, and indeed scientists modeling the problem have indicated that valid data are insufficient to complete existing models. Past and present studies have not adequately emphasized that acid precipitation is affected by a system whose spectrum covers a span from in-ground coal resources to the acidification of streams, lakes, soils, and so on, and its subsequent effects on the ecosystem. To make sound scientific judgments or to provide sound technical options for policymakers requires that the entire spectrum be examined in detail, that systematic efforts to deal with the acid rain problem be made from a credible and reliable knowledge base, and that the results be balanced, equitable, and achievable.

A large part of the knowledge base being used today is founded upon inadequate characterization of our coal resources. Many assessments of quality and quantity are 50 or more years old and reflect not only outmoded techniques and technology but also mined-out, exhausted, and abandoned mining areas. Consequently, many of the often-quoted conclusions concerning sulfur content and regulations are based on coal analyses of questionable merit.

Current areas of research in the acid-precipitation problem are indicated in the right half of figure 25.1, which is redrawn from a sketch that appeared in a special report of the Electric Power Research Institute (Moore, 1983) devoted to acid-rain research. Research efforts in these areas include identification of point sources, monitoring the problem, impact on ecosystems, and so on. The starting points for many existing studies are the powerplants where emissions of potential pollutants originate and whose emissions contribute to various atmospheric, physiochemical, biological, and hydrologic reactions and interactions.

In our view, these areas constitute only half of the system. In the left half of figure 25.1, we added three additional areas that we believe must be considered to

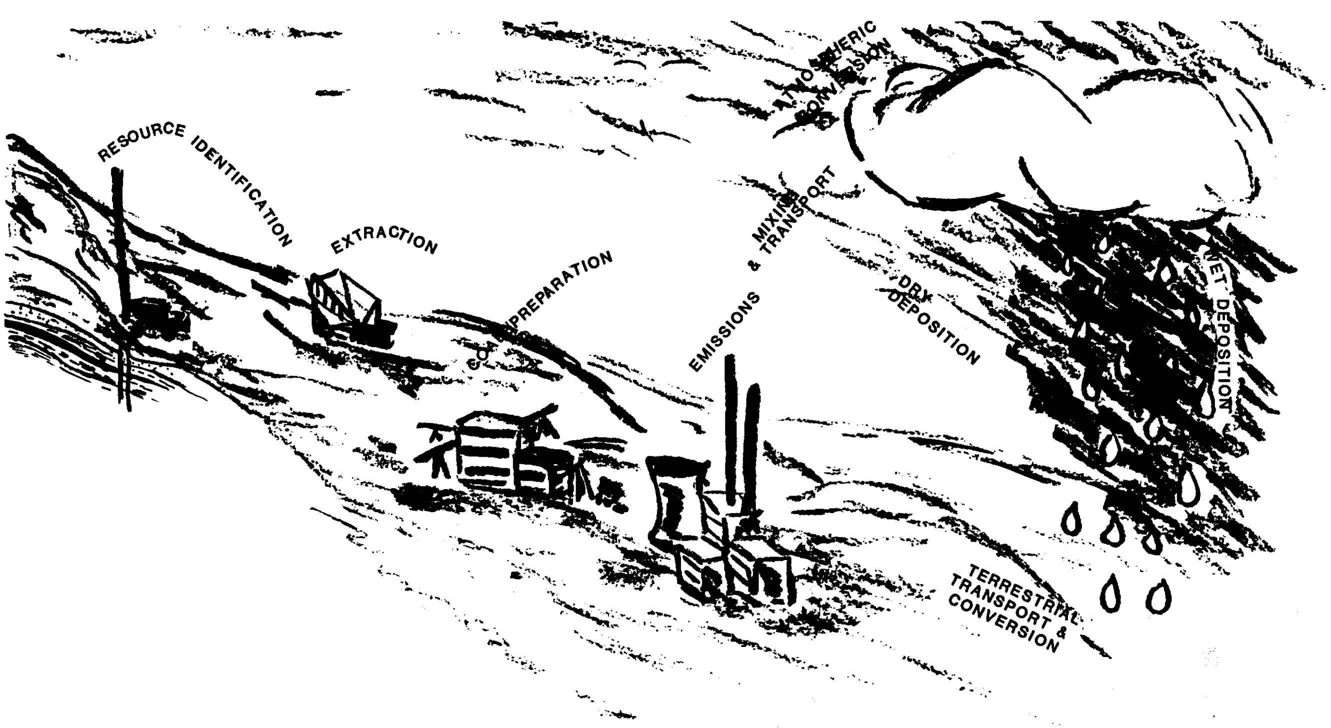


Figure 25.1. The link between resource identification, mining, and coal preparation and pollution emissions and the fate of acidic compounds in the atmosphere. From Moore, 1983.

effectively attack the acid-precipitation problem. The first area is identification and delineation of the coal resource; the second is the extraction or mining stage; and the third is the coal preparation stage. These areas represent stages of a cycle in which various options can be identified at each stage, tradeoffs made, and decisions implemented to minimize the amount of acid precipitation progenitors that will be emitted into the atmosphere. The consideration of these three additional areas should lead to more sound scientific and economic options concerning the mitigation and regulation of the emission of sulfur dioxide and other deleterious substances.

We will focus on these three areas and discuss in detail the role that coal characterization can play in addressing the acid precipitation problem. However, we first must define coal characterization or coal quality.

COAL QUALITY

An all-encompassing definition of coal quality is probably impossible to devise because quality requirements differ according to the end use of the coal. Utilities require coal that has different properties from the steel industry, whose requirements may substantially differ from those users who gasify or liquefy or use coal as a chemical feedstock (fig. 25.2). Each powerplant is uniquely designed and built for coal that has closely defined physical and chemical properties. Thus, each powerplant has different quality requirements. In times past, powerplant operators were interested only in calorific value and ash content. Later, with some encouragement from the Government, sulfur was included. Economics, burning characteristics of coal, corrosion and fouling of boiler tubes, and other concerns have expanded the list of tests in which the powerplant operator is interested. Recently, they also began to consider ash fusion temperatures; major, minor, and trace-element composition; and hardgrove grindability index. Today, powerplant operators are concerned with all of the characteristics of coal quality.

The data used to implement existing or proposed regulations are based on various sources. Careful evaluation of these sources shows the data to be incomplete, not comprehensive, not comparable, and inadequately verified. For example, much existing sulfur data cannot be related directly to in-ground resources. Analyses were done on a mixture of run-of-mine, grab, delivery, or otherwise unrepresentative types and generally were inadequately documented. Chemical analyses were made by a variety of techniques, were determined by old and new methods, and were derived from many laboratories using different standards and techniques. The results, therefore, are not representative of the coal bed or coal-bearing sequence from which they are purported to come. Credible, reproducible data are needed for all coal beds and coal-bearing regions of the United States; samples must be point located and

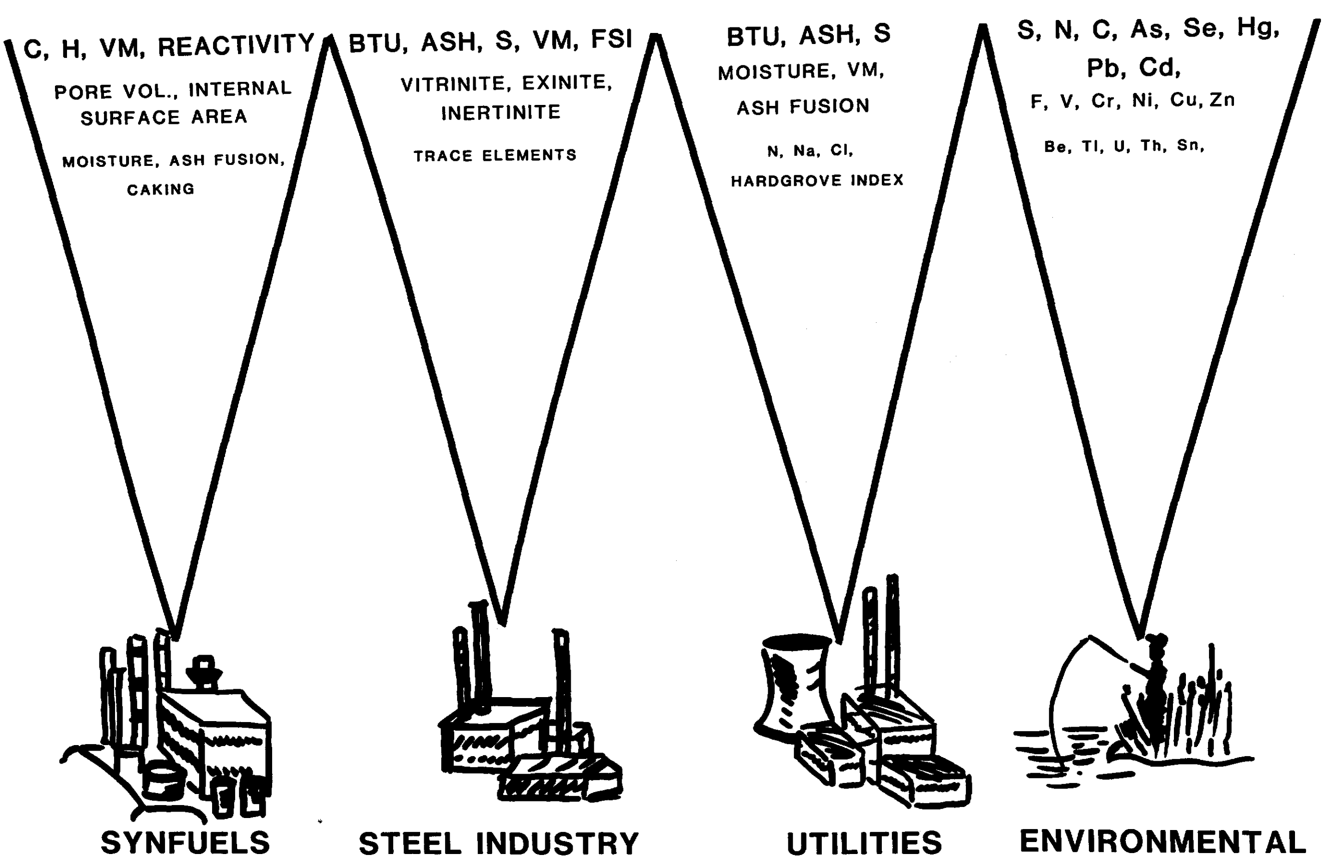


Figure 25.2. Coal-quality parameters important in coal utilization. Less common abbreviations used in this figure are VM (volatile matter), FSI (free swelling index), and pore vol. (pore volume).

correlated, and sampling procedures must be standardized. Limited data bases exist on the national and State levels, and industry possesses (confidential) data for tracts in which they have an interest. The most extensive of these data bases is resident in the U.S. Geological Survey (USGS) (table 25.1). It contains data on 128 parameters for more than 6,200 correlated coal samples—but most of those samples are from only a few beds, and we have a long way to go to obtain adequate coverage for the entire United States. In fact, this data base has data (one or more samples per coal bed per county) for only one-third of the coal resources in the U.S. Bureau of Mines' demonstrated coal-reserve base (U.S. Bureau of Mines, 1974).

Analysis of coal samples should include not only those determinations that are economically or use related but also the entire list of major, minor, and trace elements. One might ask why we should be concerned with trace levels of contaminants that most people have never heard of. The answer is that these elements are being remobilized by the mining and combustion processes and consequently are made available to the environment. Table 25.2 lists the amounts of selected elements that are mobilized as a result of the annual coal production for a typical 1,000-megawatt (MW) powerplant for the United States for the years 1978 and 2000 and for the world for the years 1978, 2000, and 1979–2000. Although the elements are present in coal in trace amounts, the large amount of coal being burned causes the potential for contamination from trace toxic elements to be great. If scrubbers are used, a proportion of the contaminants in table 25.2 will end up in the scrubber sludge, causing disposal and potential ground-water pollution problems that should not be ignored (approximately 50 percent of the U.S. population depends on ground water as a source of drinking water). The fate and consequences of the availability to the environment of volatile constituents such as arsenic, antimony, selenium, fluorine, and mercury are less known and less understood, but they are much more toxic than sulfur or nitrogen. Almost 200 tons of these five elements will be emitted annually from a typical 1,000-MW powerplant. These amounts can be altered by one to two orders of magnitude (either up or down) by selecting the appropriate coal feedstock.

Coal is a heterogeneous substance that contains both organic and inorganic elements and compounds. The two elements that most directly impact the acid-precipitation problem are sulfur and nitrogen; they also seem to be the two most frequently cited variables of concern in the acid-precipitation debate. However, other contaminants can

Table 25.1. Data items for the U.S. Geological Survey National Coal Resources Data System's USCHEM data base

1. State
2. County
3. Latitude
4. N/S
5. Longitude
6. E/W
7. AAPG[1] province
8. Coal province
9. Region
10. Field
11. District
12. Formation
13. Group
14. Bed
15. Member
16. Zone
17. Depth
18. Sample thickness
19. System
20. Series
21. Location name
22. Quadrangle
23. Collector
24. Field ID No.
25. Date
26. Estimated rank
27. Rank (class; calc'd.)
28. Rank (group; calc'd.)
29. ID (alpha)
30. ID (numeric)
31. Labcode
32. Sample type
33. Analysis type
34. Values represent
35. NCRDS check
36. Calorific value
37. Ash deformation temp.
38. Ash softening temp.
39. Ash fluidization temp.
40. Free swelling index
41. Moisture
42. Volatile matter
43. Fixed carbon
44. BMASH (750 °C)
45. Carbon
46. Oxygen
47. Hydrogen
48. Nitrogen
49. Sulfur (total)
50. Sulfur (sulfate)
51. Sulfur (pyritic)
52. Sulfur (organic)
53. Air-dried loss
54. USGSASH (525 °C)
55. SiO_2
56. Al_2O_3
57. CaO
58. MgO
59. Na_2O
60. K_2O
61. Fe_2O_3
62. MnO
63. TiO_2
64. P_2O_5
65. SO_3
66. Ag - silver
67. As - arsenic
68. Au - gold
69. B - boron
70. Ba - barium
71. Be - beryllium
72. Bi - bismuth
73. Br - bromine
74. Cd - cadmium
75. Ce - cerium
76. Cl - chlorine
77. Co - cobalt
78. Cr - chromium
79. Cs - cesium
80. Cu - copper
81. Dy - dysprosium
82. Er - erbium
83. Eu - europium
84. F - fluorine
85. Ga - gallium
86. Gd - gadolinum
87. Ge - germanium
88. Hf - hafnium
89. Hg - mercury
90. Ho - holmium
91. In - indium
92. Ir - iridium
93. La - lanthanum
94. Li - lithium
95. Lu - lutetium
96. Mn - manganese
97. Mo - molybdenum
98. Nb - niobium
99. Nd - neodymium
100. Ni - nickel
101. Os - osmium
102. Pb - lead
103. Pd - palladium
104. Pr - praseodymium
105. Pt - platinum
106. Rb - rubidium
107. Re - rhenium
108. Rh - rhodium
109. Ru - ruthenium
110. Sb - antimony
111. Sc - scandium
112. Se - selenium
113. Sm - samarium
114. Sn - tin
115. Sr - strontium
116. Ta - tantalum
117. Tb - terbium
118. Te - tellurium
119. Th - thorium
120. Tl - thallium
121. Tm - thulium
122. U - uranium
123. V - vanadium
124. W - tungsten
125. Y - yttrium
126. Yb - ytterbium
127. Zn - zinc
128. Zr - zirconium

[1] American Association of Petroleum Geologists.

act synergistically to either accelerate or retard reactions involving these variables, but these constituents have not been extensively studied. More studies of these trace contaminants are needed because we are dealing with a multivariant system.

COAL-RESOURCE IDENTIFICATION AND DELINEATION

Figure 25.3 shows the coal basins of the United States. The first stage of a comprehensive program to abate acid precipitation is the identification and delineation of the remaining, in-ground coal resources of North America. It is common knowledge that almost 4 trillion tons of coal resources have been identified or speculated to occur in the United States (Averitt, 1975). Moreover, the U.S. Bureau of Mines (1974) and the U.S. Department of Energy (1981) have concluded that 438 to 474 billion tons of these resources are economically recoverable by existing technology. The quantity is not the most important factor, but the magnitude of the numbers causes much misunderstanding among decisionmakers and even among scientists and technical people studying U.S. coal.

The most important aspects in the discussion of coal resources, once it is concluded that there is a lot of coal, are the quality of that coal, the distribution and occurrence of the high-quality coal, and the methods or techniques that

Table 25.2. Quantities of trace elements mobilized as a result of coal production
[Modified from Zubovic and others, 1979. Data are in tons; MW, megawatts]

Element	Typical 1,000-MW plant (annual production)	United States		World		
		1978	2000	1978	2000	1979–2000
Sulfur	30,500	7×10^6	19×10^6	41×10^6	105×10^6	1700×10^6
Arsenic	13.7	3,300	8,400	19,000	47,000	770,000
Beryllium	3.8	910	2,300	5,100	13,000	210,000
Cadmium	0.4	91	230	510	1,300	21,000
Cobalt	9.4	2,270	5,800	13,000	33,000	530,000
Chromium	25.3	6,110	15,000	34,000	87,000	1,400,000
Copper	32.3	7,800	20,000	43,000	110,000	1,800,000
Fluorine	174.2	42,000	110,000	230,000	590,000	9,700,000
Mercury	0.24	59	150	328	843	14,000
Lithium	22.4	5,400	14,000	30,000	77,000	1,300,000
Manganese	66.3	16,000	41,000	91,000	230,000	3,800,000
Molybdenum	5.0	1,200	3,000	6,500	17,000	270,000
Nickel	19.5	4,700	12,000	26,600	68,000	1,100,000
Lead	19.1	4,600	12,000	25,000	65,000	1,100,000
Antimony	1.6	380	950	2,100	5,400	88,000
Selenium	4.6	1,100	2,800	6,200	16,000	250,000
Uranium	3.5	850	2,100	4,700	12,000	200,000
Vanadium	40.6	9,800	25,000	54,000	140,000	2,300,000
Zinc	37.7	9,100	23,000	51,000	130,000	2,100,000

exist to improve the quality of the coal to make it meet usage and environmental requirements. The notion of the quantity of U.S. coal is very much like arguments over clean air. It is not the quantity of air we are immediately concerned about (it being assumed that there is a lot of it), but the quality of that air, the concentration and distribution of its pollutants, and how to maintain air quality without disrupting the industrial base of the nation that are of interest. Figure 25.4 illustrates the present state of our resource knowledge when considering coal-quality parameters. Each vertical bar represents a concentration bracket for sulfur, and the height of the bar represents the tonnage of coal having the specified sulfur content in the U.S. Bureau of Mines demonstrated reserve base. Although differences in the concentration bands exist among basins, the "unknown" bar is uniformly large for all basins.

At present, our knowledge and understanding of the sulfur and nitrogen concentration and distribution in U.S. coals are better than for any other contaminant, and yet they are vague and very general if one considers the in-ground coal resources. For example, one frequently hears such statements as, "Appalachian coal is medium sulfur"; "Midcontinent coal is high sulfur"; "Western coal is low sulfur."

These gross generalizations are misleading and oversimplified because we know that, in parts of the midcontinent and Appalachian coal fields, a potential exists for large quantities of low-sulfur, high-quality coal. It also is generally known, but little publicized, that large areas within these coal basins are unexplored and little quality characterization exists for them. In the eastern U.S. coal fields, unexplored areas are located away from coal-field margins. Figure 25.5 outlines the Pittsburgh coal bed; the dots mark the locations of samples for which analytical data are stored in the USGS USCHEM data base. The paucity of data in the center of the coal field is apparent. What is needed is to identify, delineate, and characterize the coal in these unexplored areas. Moreover, the Pittsburgh coal bed is one of the best characterized coal beds in the United States; for most other coal beds, the distribution of analyses is worse than that depicted in figure 25.5. There also is a need to characterize coal beds in areas being mined so that selected mining and blending can be used to reduce sulfur and nitrogen contents to acceptable levels.

Characterization of in-ground resources allows development of viable options concerning feedstock specifications and sources; it also allows fundamental decisions to be made concerning extraction methods and whether to clean, blend, crush, or size the coal before combustion in powerplants. This kind of knowledge can lead to the development of models that will allow prediction of the potential SO_2 emissions for a region, as well as for a single power facility, and for the short-, medium-, and long-term future.

SELECTIVE MINING AND BENEFICIATION

The second stage of a comprehensive program for the abatement of acid precipitation involves improvements in the extraction and beneficiation of coal. In-ground coal-

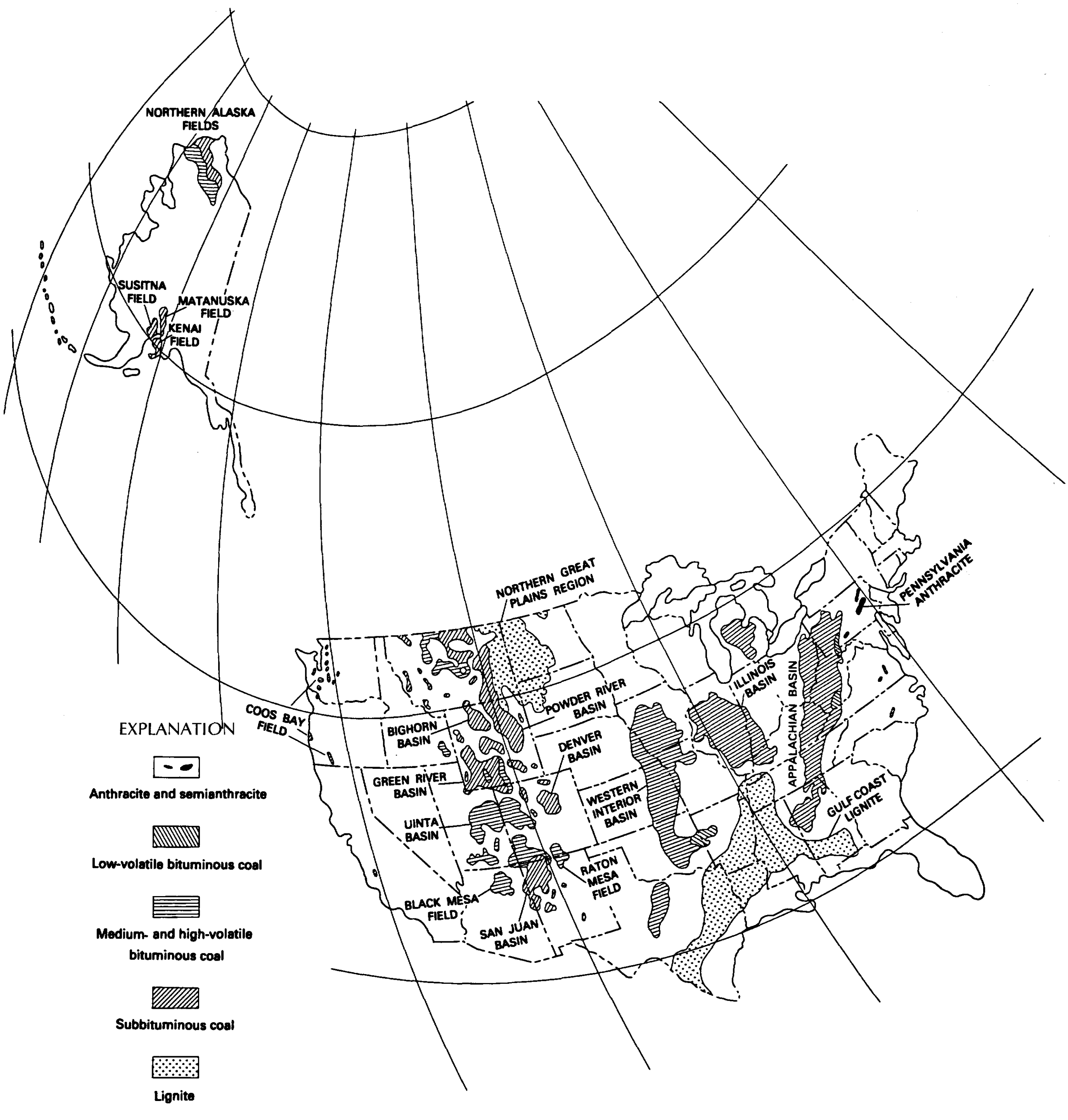


Figure 25.3. Coal basins of the continental United States. From Garbini and Schweinfurth (1986).

resource characterization will provide options and allow a greater range of decisions concerning selective mining of several coal beds or blending of coal from one or more beds within the same mine or from several mines within the coal field. Regional knowledge and site-specific data can frequently allow, through blending, an opportunity to reduce the sulfur and nitrogen contents to acceptable levels before combustion without cleaning the coal or scrubbing the emissions. This is especially beneficial for older powerplants whose economic situation will not justify the retrofit installation of scrubbers. If the adaptation of low-sulfur and low-nitrogen coal sources can be gradual, the disruption of the mining industry will be minimal.

Figure 25.6 illustrates how selective mining can help. This actual example shows a mine in an eastern coal field containing bed A and three benches of bed B; the sulfur and ash contents are shown. Within 200 feet of stratigraphic section and 1 mile distance, sulfur content ranges from 1.52 to 15.0 percent, and ash content ranges from 9.09 to 18.29 percent.

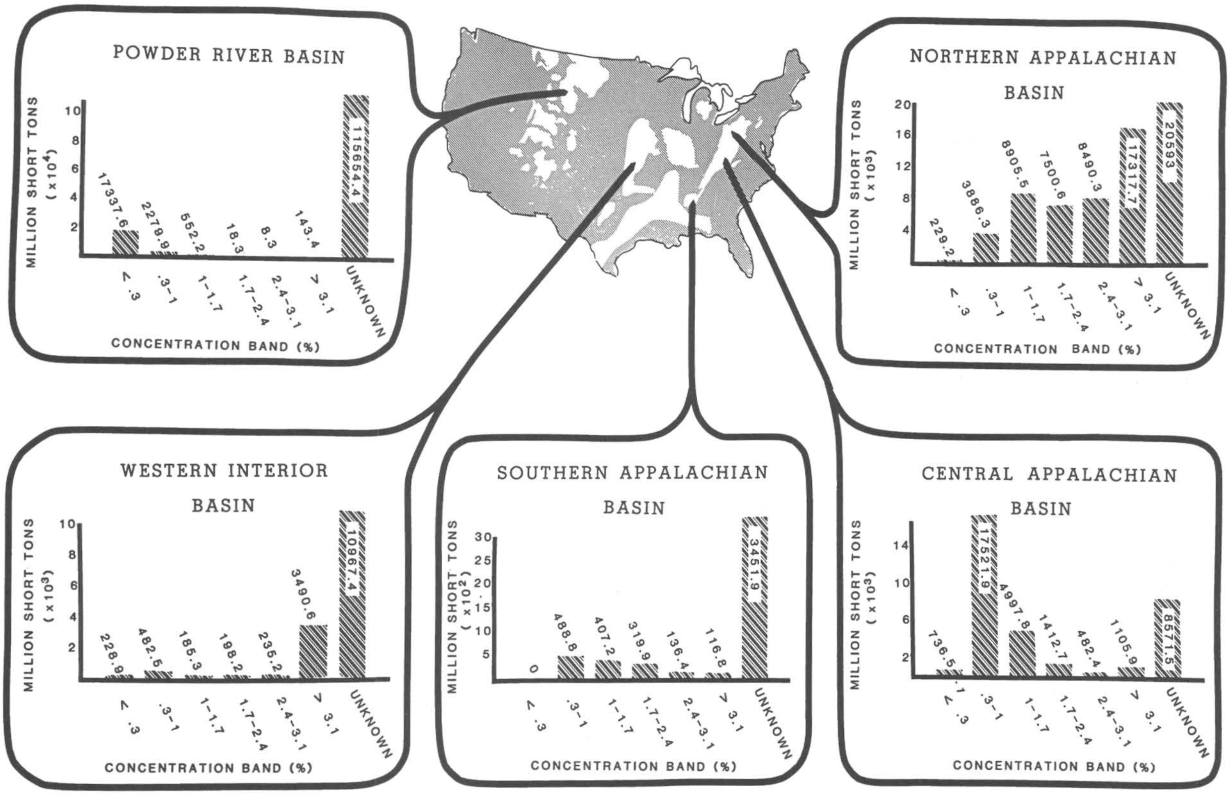


Figure 25.4. Total sulfur plotted against demonstrated reserve base of coal in the United States. Sulfur data are divided into seven bands and related to reserve tonnage.

PREPARATION AND BENEFICIATION

The third stage in the proposed program, coal preparation, has been a standard procedure in the coal industry for many years. Upgrading coal quality with selective beneficiation methods helps to meet the specifications of the end user. Most of these specifications are limited to higher calorific value and lower sulfur and ash contents than naturally occur in a coal bed; these objectives are accomplished by using heavy liquid media, crushing, sizing, screening, and blending (fig. 25.7). The efficiency of the entire coal-preparation process is predicated on the quality of the in-ground coal resources. Changes in the physical and chemical properties of the feedstock change that efficiency. Furthermore, it should be emphasized that most cleaning processes are not designed to deal with organically bound elements. Virtually all of the nitrogen and approximately half of the sulfur in coal are organically bound. Chemical techniques are more successful in removing organic sulfur, but these have seen only limited experimental application because of the high cost. In addition, finely divided minerals that are intimately mixed with organic matter (the source of inherent ash) cannot be removed by normal cleaning techniques; fine grinding methods could provide a technical breakthrough. More than 150 minerals from coal have been identified (Gluskoter, 1978; Finkelman, 1980; Gluskoter and others, 1981). Some of these are listed in table 25.3.

Coal is an inhomogeneous material that changes laterally (regionally) and vertically (stratigraphically). As a result, coal-resource characterization is needed to anticipate the natural changes in coal quality and to estimate the rate of change. In addition, basic information on coal structure and the modes of occurrence of trace contaminants can contribute to the design of cleaning processes to eliminate much of the contamination from toxic elements. One of the ironies of many coal characterizaton studies is that they were performed on coal that had already been mined. Many environmental regulations and mitigation measures are based solely on data for coal that is no longer there.

We have shown that, with increased emphasis on coal cleaning and the development of new and improved cleaning methods, sulfur, nitrogen, and other contaminant concentrations can be reduced. This reduction will lead to a cleaner fuel being introduced into the powerplants and less resultant contamination of the atmosphere. We also have shown that, by carefully characterizing the resource, by taking greater care in mining, and by cleaning and blending coals, the need for scrubbers will be reduced considerably or be made unnecessary.

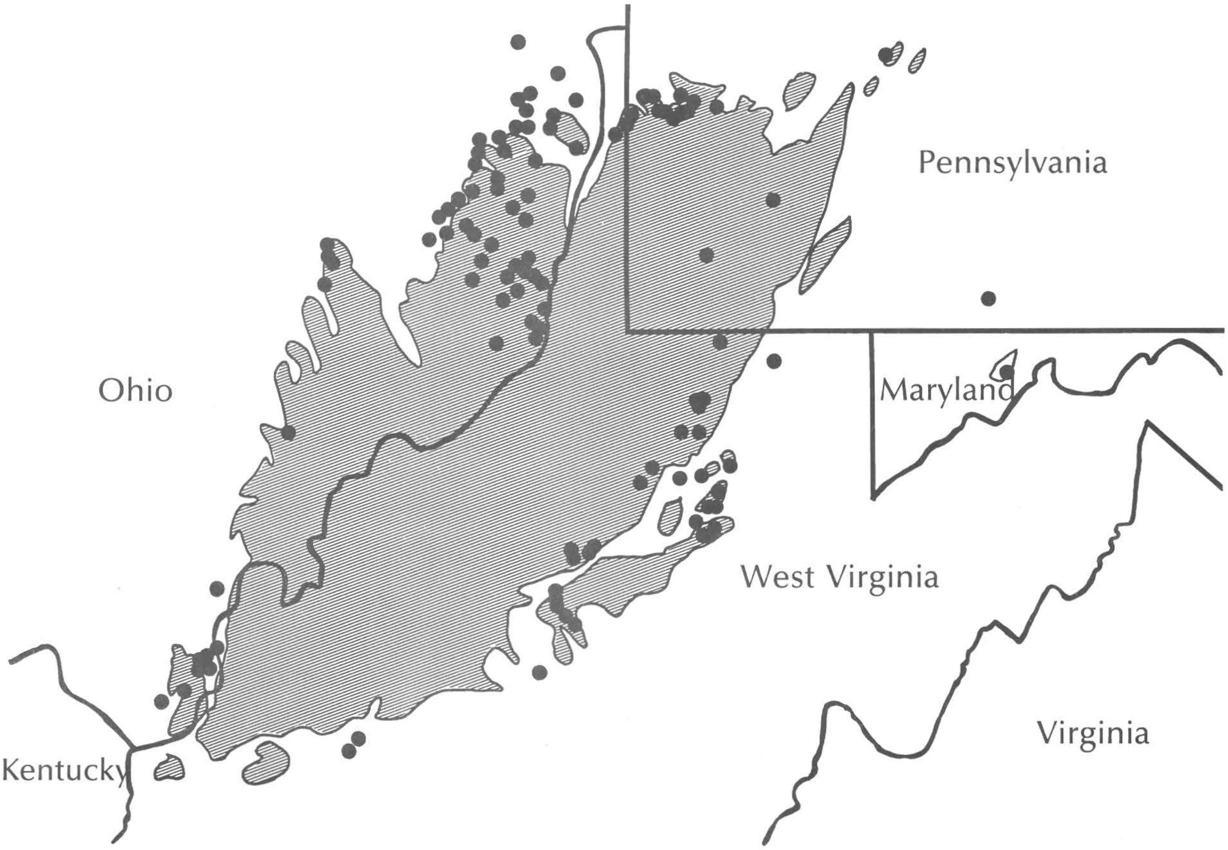


Figure 25.5. Outline of the Pittsburgh coal bed showing sample locations (black circles) for which analytical data are stored in the U.S. Geological Survey's USCHEM data base.

CURRENT SULFUR EMISSION STANDARDS

As of 1984, the Environmental Protection Agency (EPA) standard allowed the emission of 1.2 pounds of SO_2 per million Btu. In 1980, this standard permitted an estimated emission of 15,908,000 tons of SO_2 (Argonne National Laboratory, 1983). Bills introduced in the U.S. Congress in 1981 and 1982 require future total SO_2 emissions to be reduced by 6.5 to 13 million tons per year or 0.6 pounds of SO_2 per million Btu (Armbruster and others, 1983). Armbruster and others (1983) and Brady (1983) estimate that the cost of meeting these standards ranges from \$3 billion to \$12 billion annually for a reduction of 8 million to 10 million tons of SO_2 per year. These estimates are based on several assumptions, but one that bears some discussion is a commonly held misconception that a switch to low-sulfur western coal will solve the problem. One needs to examine this option with some care; most low-sulfur western coal also is much lower in Btu's than midwestern and eastern U.S. coal. Figure 25.8 shows that, when considered on a Btu basis, coal having equal or lower sulfur and ash contents can be found in the East. Careful and systematic characterization of all U.S. coal resources may reveal more low-sulfur, high-Btu coal that can directly meet the SO_2 reductions or that can be cleaned or blended to meet proposed reduced standards.

At present, it is difficult to obtain a specific estimate of the magnitude of the acid-precipitation problem because our data base on sulfur and nitrogen contents in coal allows us to estimate only on large regional areas, and, as we have demonstrated, most of these estimates are for coal that has already been mined or that is being mined. There are no credible and reliable data on the sulfur and nitrogen contents of coal that will be mined in the long term because little exploration or analysis has been undertaken in these areas.

EFFECT OF CHANGES IN THE SO_2 EMISSION STANDARD

Recent studies by the Kentucky Geological Survey (Cobb and others, 1982, 1983) estimated the impact of reducing the present 1.2 pounds SO_2 per million Btu standard on Kentucky's coal resources (see fig. 25.9). By using the EPA standards for both operating and new

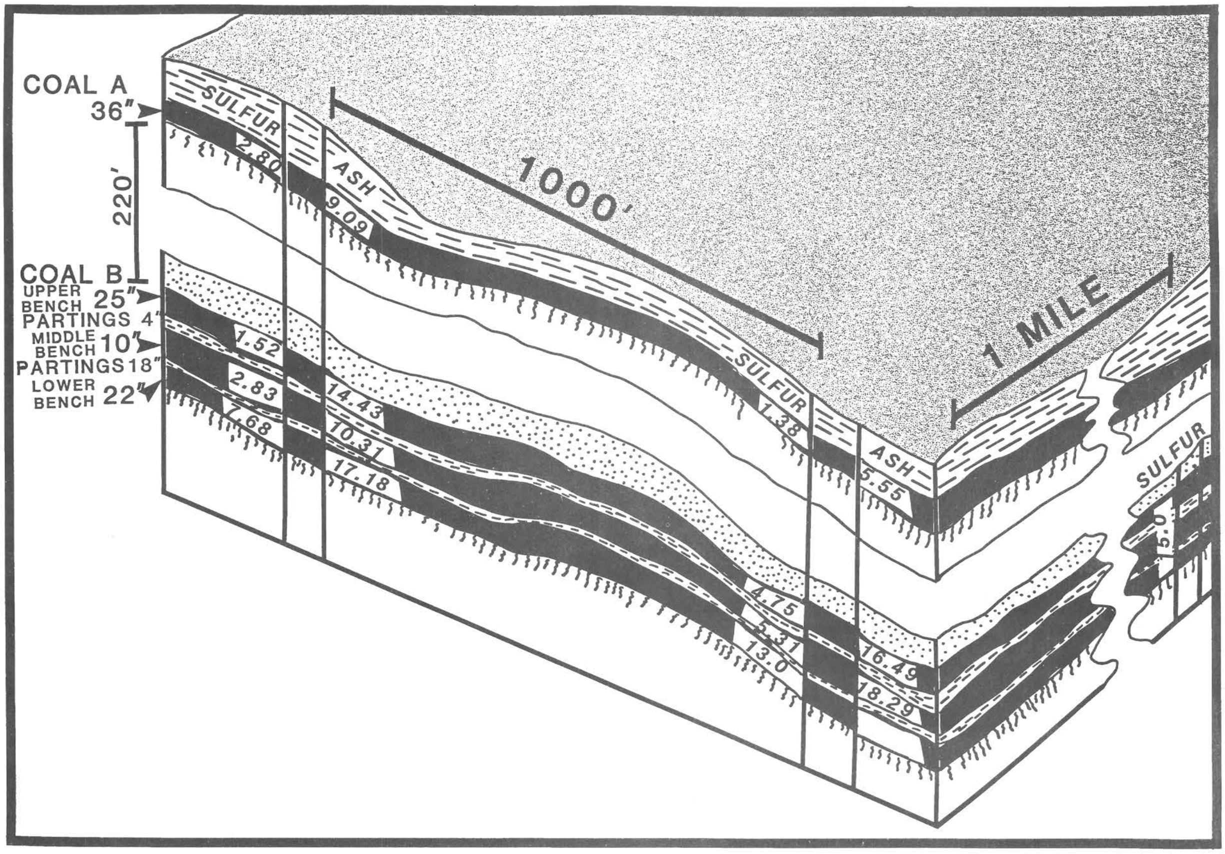


Figure 25.6. Example of variability of sulfur and ash (in percent) within a mine in an eastern coal field. (Courtesy of P.C. Lyons, U.S. Geological Survey.)

powerplants (1.2 and 0.6 pound SO_2 per million Btu, respectively) and a probability model, Cobb and others predicted that approximately 50 percent of the coal resources in eastern Kentucky is in compliance at the 1.2-pound standard, whereas only 1 percent of the resources is estimated by the model to be in compliance at the 0.6-pound standard. Their studies show that lowering the standard will bring hardship on the coal industry of the leading coal-producing State in the Nation. A larger and more detailed data base may identify lower sulfur resources and, combined with cleaning and blending, may aid in greatly reducing the SO_2 levels, although it is unlikely that the reductions will be sufficient to satisfy the 0.6-pound standard.

COAL-QUALITY MODELS AND REGULATIONS

Modeling coal quality can greatly enhance our ability to predict the quantities of low-, medium-, and high-sulfur coal still available at local, regional, and national scales. The physical, biological, and chemical conditions of the ancient peat swamp, and their interaction with the indigenous plant materials, led to the formation of specific types of peat and hence to specific types of coal. Environmental influences such as the proximity to marine conditions (sources of sulfur), the types of plants contributing to the swamp, and geochemical influences such as acidity, redox potential, and the type of sulfur compounds present affect the characteristics of the peat and the amount of sulfur that ends up in the coal. For example, Dorofeev (1974) concluded that typical sulfur contents of Carboniferous coals of the Donetz in the U.S.S.R. varied according to their environment of deposition (table 25.4).

The variations in coal properties affected by the depositional environment may have been local or widespread. Many of the factors influencing the quality of coal have left their fingerprints in the geologic record and, with the proper geologic controls, can be used to develop models for the prediction of coal quality in areas where analytical data are lacking. The danger lies in making broad generalizations without adequate models or supporting evidence.

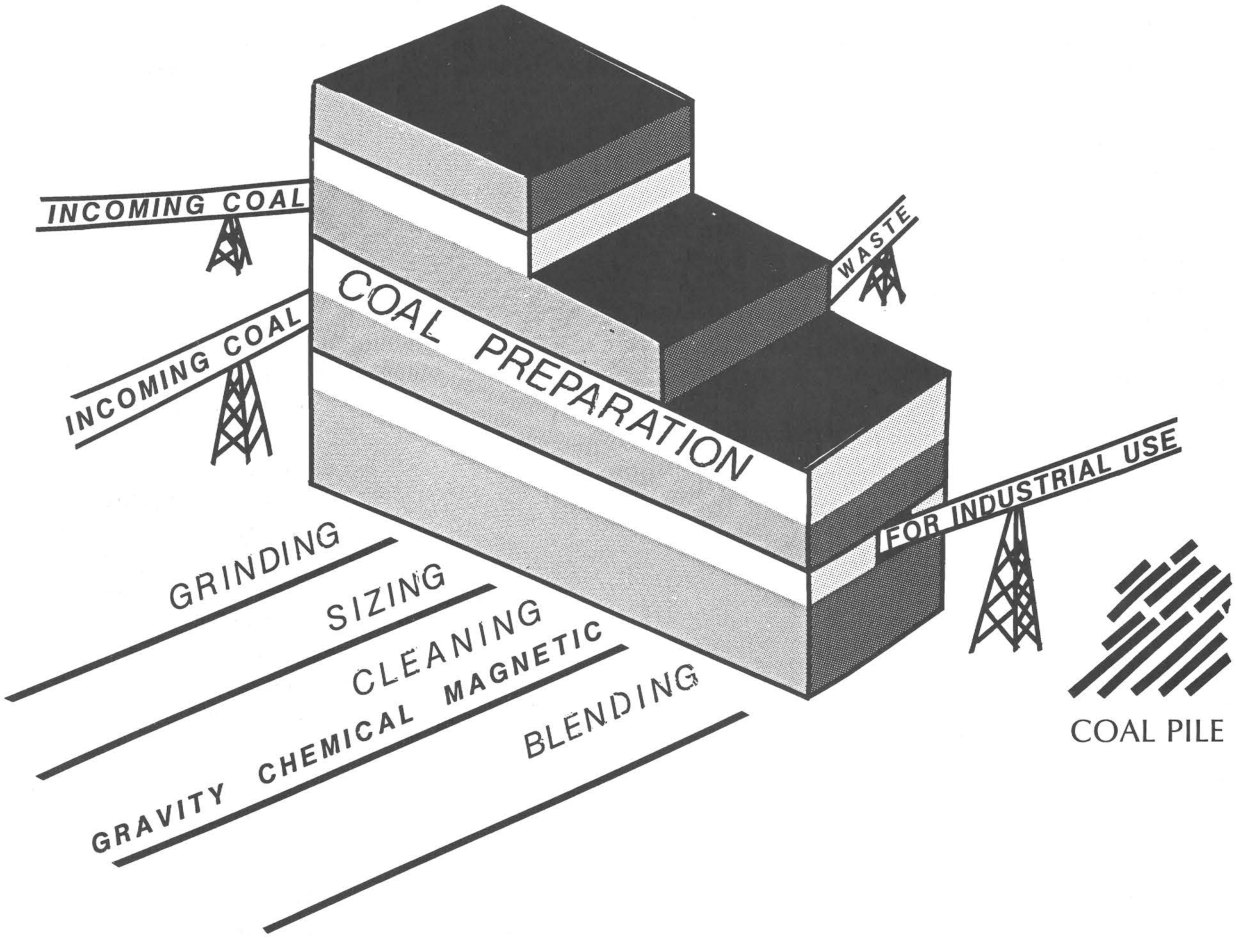


Figure 25.7. Standard procedures in coal preparation.

CONCLUSIONS

Regulations can be based on coal-quality models if the models are based on sound data and sound scientific judgment and if the models are applied properly. Models based on inadequate or inaccurate data can lead only to unsound regulations at best and, at worst, will produce extreme hardships on a large portion of society.

In conclusion, the Nation needs a comprehensive program to provide a balance among coal characterization, selective mining, coal cleaning, scrubbers, and the use of new and existing powerplants. It is time to stop dealing with only one-half of the spectrum; it is time to gather some very basic data that will lead to the development of more options (other than scrubbers) to address the acid-rain problem.

Table 25.3. Minerals known to occur naturally in coal

[From Gluskoter and others, 1981; Mineral formulas according to Bates and Jackson, 1987]

Mineral	Formula
Clay minerals	
Montmorillonite	$Al_2Si_4O_{10}(OH)_2H_2O$
Illite-sericite	$KAl_2(AlSi_3O_{10})(OH)_2$
Kaolinite	$Al_4Si_4O_{10}(OH)_4$
Halloysite	$Al_2Si_2O_{10}(OH)_4H_2O$
Chlorite (prochlorite, penninite)	$Mg_6AlSi_3O_{10}(OH)_8$
Mixed-layer clay minerals	
Sulfide minerals	
Pyrite	FeS_2
Marcasite	FeS_2
Sphalerite	ZnS
Galena	PbS
Chalcopyrite	$CuFeS_2$
Pyrrhotite	$Fe_{1-x}S$
Arsenopyrite	$FeAsS$
Millerite	NiS
Carbonate minerals	
Calcite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Siderite	$FeCO_3$
Ankerite	$Ca(Fe,Mg,Mn)(CO_3)_2$
Witherite	$BaCO_3$
Sulfate Minerals	
Barite	$BaSO_4$
Gypsum	$CaSO_4 \cdot 2H_2O$
Anhydrite	$CaSO_4$
Bassanite	$CaSO_4 \cdot 1/2H_2O$
Jarosite	$KFe_3(SO_4)_2(OH)_6$
Szomolnokite	$FeSO_4 \cdot H_2O$
Rozenite	$FeSO_4 \cdot 4H_2O$
Melanterite	$FeSO_4 \cdot 7H_2O$
Coquimbite	$Fe_2(SO_4)_3 \cdot 9H_2O$
Roemerite	$Fe^{+2}Fe^{+3}(SO_4)_4 \cdot 14H_2O$
Mirabilite	$Na_2SO_4 \cdot 10H_2O$
Kieserite	$MgSO_4 \cdot H_2O$
Sideronatrite	$Na_2Fe^{+3}(SO_4)_2(OH) \cdot 3H_2O$
Chloride minerals	
Halite	$NaCl$
Sylvite	KCl
Bischofite	$MgCl_2 \cdot 6H_2O$
Silicate minerals	
Quartz	SiO_2
Biotite	$K(Mg,Fe^{+2})_3(Al,Fe^{+3})Si_3O_{10}(OH)_2$
Zircon	$ZrSiO_4$
Tourmaline	$(Na,Ca)(Mg,Fe^{+2},Fe^{+3},Al,Li)_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$
Garnet	$(Ca,Mg,Fe^{+2},Mn^{+2})_3(Al,Fe^{+3},Mn^{+3},V^{+3},Cr)_2(SiO_4)_3$
Kyanite	Al_2SiO_5
Staurolite	$(Fe,Mg)_2Al_9Si_4O_{23}(OH)$
Epidote	$Ca_2(Al,Fe)_3Si_3O_{12}(OH)$
Albite	$NaAlSi_3O_8$
Sanidine	$KAlSi_3O_8$
Orthoclase	$KAlSi_3O_8$
Augite	$(Ca,Na)(Mg,Fe^{+2},Al)(Si,Al)_2O_6$
Hornblende	$(Ca,Na)_{2-3}(Mg,Fe^{+2},Fe^{+3},Al)_5(Al,Si)_8O_{22}(OH)_2$
Topaz	$Al_2SiO_4(F,OH)_2$
Oxides and hydroxides	
Hematite	Fe_2O_3
Magnetite	$(Fe,Mg)Fe_2O_4$
Rutile	TiO_2
Limonite	$FeO \cdot OH \cdot nH_2O$
Goethite	$FeO(OH)$
Lepidocrocite	$FeO(OH)$
Diaspore	$AlO(OH)$
Phosphate minerals	
Apatite (fluorapatite)	$Ca_5(PO_4CO_3)_3(F,OH,Cl)$

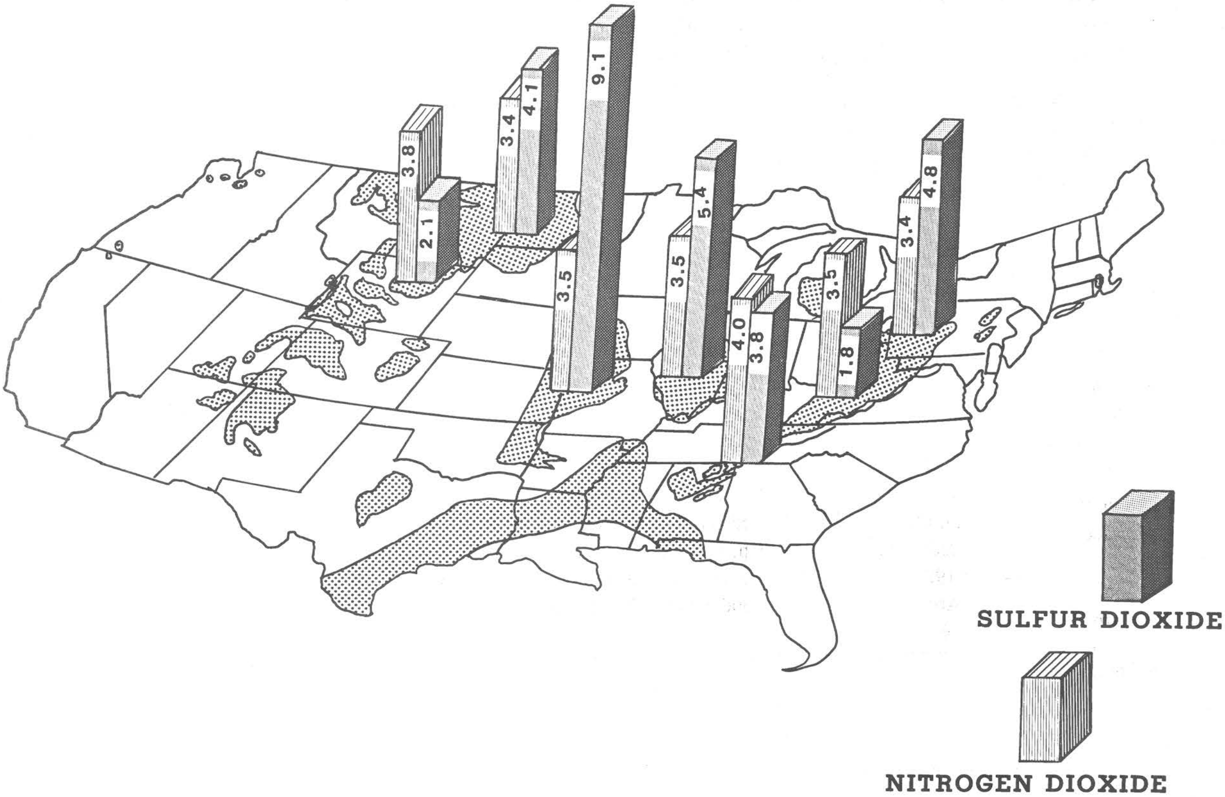
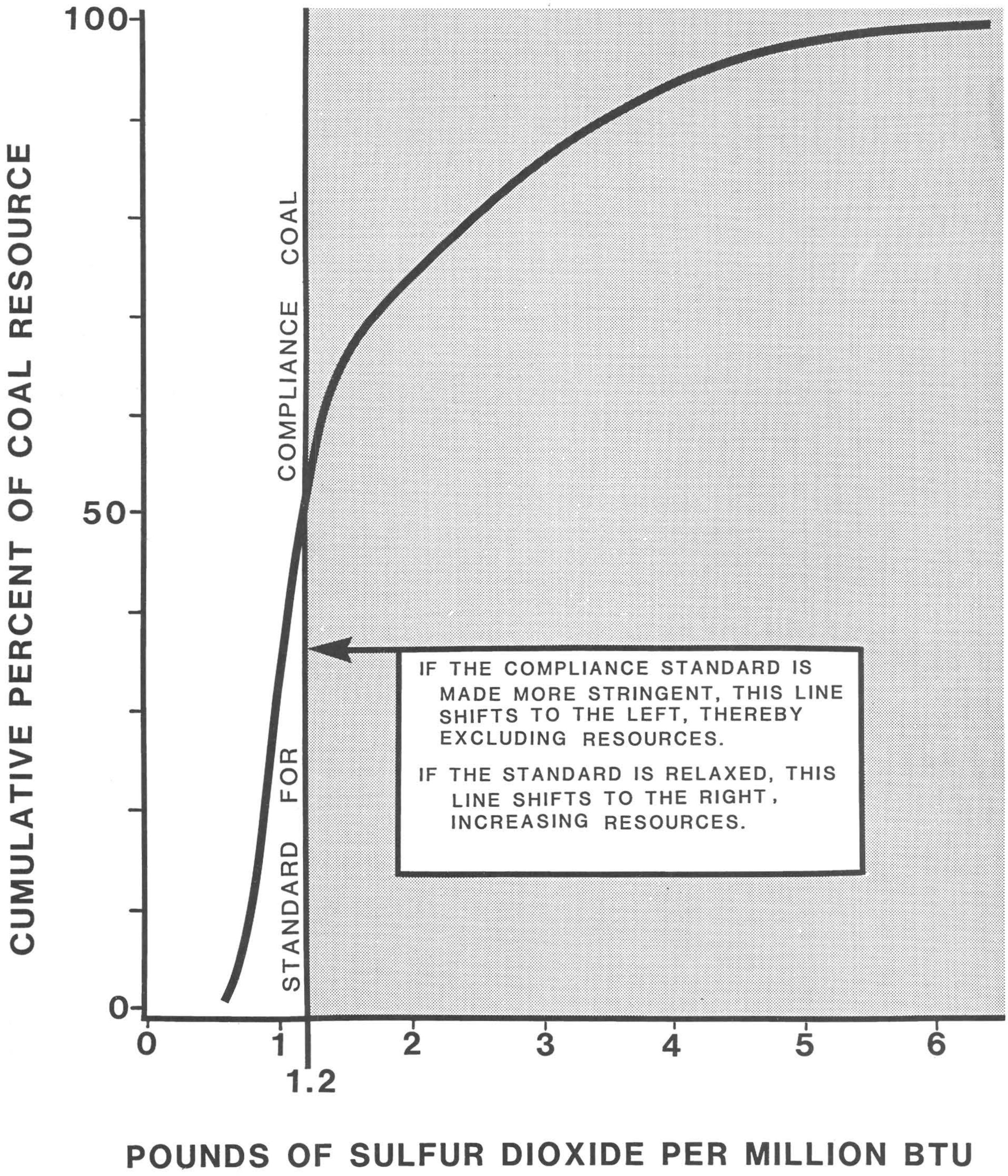


Figure 25.8. Nitrogen dioxide and sulfur dioxide concentration (in percent) in U.S. coal. Stippled areas represent coal basins.

Table 25.4. Relation between sulfur and depositional environment in the Donetz basin, U.S.S.R.

[From Dorofeev, 1974]

Depositional location	Typical sulfur content (percent)
Coastal swamps on continental margin	1.6
Coastal swamps on continental margin having weak marine influence	2.2
Coastal swamps on marine side	3.4
Swamps having prolonged marine exposure	3.9



IF THE COMPLIANCE STANDARD IS MADE MORE STRINGENT, THIS LINE SHIFTS TO THE LEFT, THEREBY EXCLUDING RESOURCES.

IF THE STANDARD IS RELAXED, THIS LINE SHIFTS TO THE RIGHT, INCREASING RESOURCES.

Figure 25.9. Impact of changing the present compliance standard on Kentucky's coal resources.

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26. Overview of the Salt and Agricultural Drainage Problem in the Western San Joaquin Valley, California

By Marc A. Sylvester

INTRODUCTION

Background

Agricultural production in irrigated areas of the western San Joaquin Valley California is affected by waterlogging of soils and salt accumulation in the crop root zone (fig. 26.1). Since 1960, subsurface drains have been installed to remove water and salts from about 85,000 acres of affected farmland. These waters and salts are discharged to surface drains and irrigation-supply canals that deliver water to farms, wetlands, and Kesterson Reservoir within Kesterson National Wildlife Refuge (fig. 26.2). Water in the wetlands eventually discharges by surface flow or seepage to the San Joaquin River, which flows into the San Francisco Bay and delta.

By 1982, the flow into Kesterson Reservoir was primarily subsurface agricultural drainage water. In 1982, the U.S. Fish and Wildlife Service (USFWS) noted high concentrations of selenium (30 parts per million (ppm), wet weight) in fish from Kesterson Reservoir and the San Luis Drain (Ohlendorf, 1984a; Saiki, 1986). In 1983, the USFWS noticed a fish kill in Kesterson Reservoir and the San Luis Drain (Saiki, 1986). In 1983 and 1984, the USFWS observed high incidences of mortality, birth defects, and decreased hatching rates in waterfowl using Kesterson Reservoir. These effects were attributed to selenium toxicity on the basis of the high concentrations of selenium in waterfowl using the reservoir (averaged greater than 60 ppm, dry weight) and morphological and physiological symptoms of toxicity (Ohlendorf, 1984a,b; Ohlendorf and others, 1986). Concentrations of selenium in waterfowl, from wetlands south of Kesterson National Wildlife Refuge that receive a mixture of drain water, irrigation supply water, and surface-return water, were generally intermediate to those found in waterfowl from Volta State Wildlife Area (averaged less than 5 ppm, dry weight), which does not receive drain water, and Kesterson Reservoir (Ohlendorf, 1984b; Ohlendorf and Hothem, 1985).

The main resource management questions are how waterlogging of soils can be prevented and how salts and toxic constituents, such as selenium, that have accumulated in the soils, water, and biota of the western San Joaquin Valley can be controlled to allow for continued agricultural use of the land without adversely affecting wildlife, human health, and beneficial uses of surface and ground waters.

Role of the U.S. Geological Survey

The role of the U.S. Geological Survey (USGS) as a scientific, fact-finding agency is to help provide the information that resource-management agencies (U.S. Bureau of Reclamation, USFWS, and State agencies) need to make informed and technically sound decisions to solve the salt and drainage problem. Since the early 1900's, the USGS has been studying the San Joaquin Valley and has published several reports about the geology, hydrology, and water quality of the valley. The USGS involvement in the salt and drainage problem began in the early summer of 1983 when the USFWS asked the USGS to test drainage water in the San Luis Drain for selenium and other constituents. Since then, the USGS has developed a program of interrelated and coordinated studies to determine the source, distribution, mobilization, transport, and fate of selenium and other constituents in the waters and soils of the western San Joaquin Valley.

IMPORTANT GEOHYDROLOGIC AND AGRICULTURAL CONDITIONS

A combination of factors appears to have produced the selenium toxicity at Kesterson National Wildlife Refuge. These factors are:

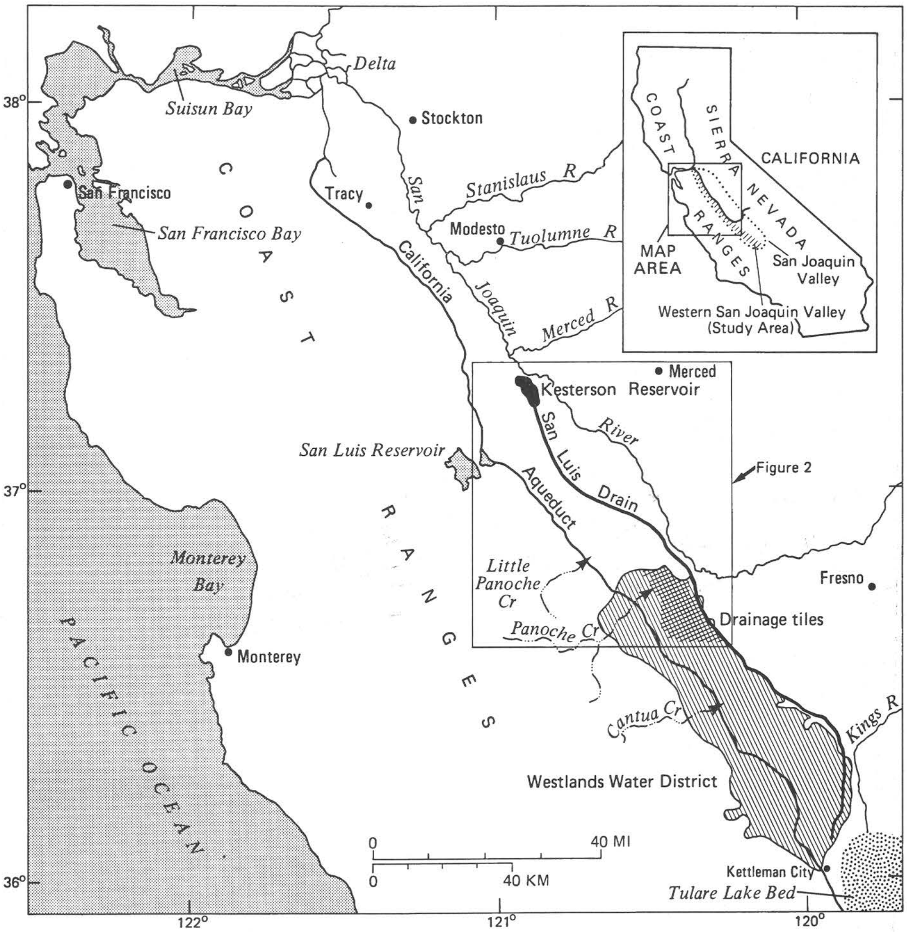

Figure 26.1. Location and main features of the study area, western San Joaquin Valley, Calif.

1. A geologic source of selenium in the Coast Ranges to the west (fig. 26.3).
2. Transport of salts containing selenium from the Coast Ranges to the alluvial fans of the western San Joaquin Valley by erosion and rainfall runoff.
3. Concentration of salts containing selenium in soils of the western San Joaquin Valley due to an arid climate (about 90 inches of evaporation and less than 10 inches of precipitation) (fig. 26.4).
4. Irrigation of crops by methods that are designed to flush salts from the soil.
5. Accumulation of flushed salts and percolated irrigation water above a clay layer 10–70 feet below land surface, present at certain locations in the western San Joaquin Valley (fig. 26.5).
6. Installation of subsurface drainage systems to remove accumulated water and salts above the clay layer mentioned in No. 5.
7. Transport of drainage water to Kesterson Reservoir via the San Luis Drain.
8. Bioaccumulation of selenium in the food chain. Kesterson Reservoir did not receive large quantities of agricultural drainage water until 1981. Prior to 1981, most of the water delivered to Kesterson Reservoir was irrigation supply and surface-return water. Apparently, it took a year or two for selenium in Kesterson Reservoir to bioaccumulate in the food chain to concentrations that caused the toxicity observed from 1983 to present.

INITIAL RESULTS OF THE USGS STUDIES

Initial results of USGS studies have helped define the source and distribution of selenium and other inorganic constituents in the waters and soils of the western San Joaquin Valley (Deverel and others, 1984; Izbicki, 1984;

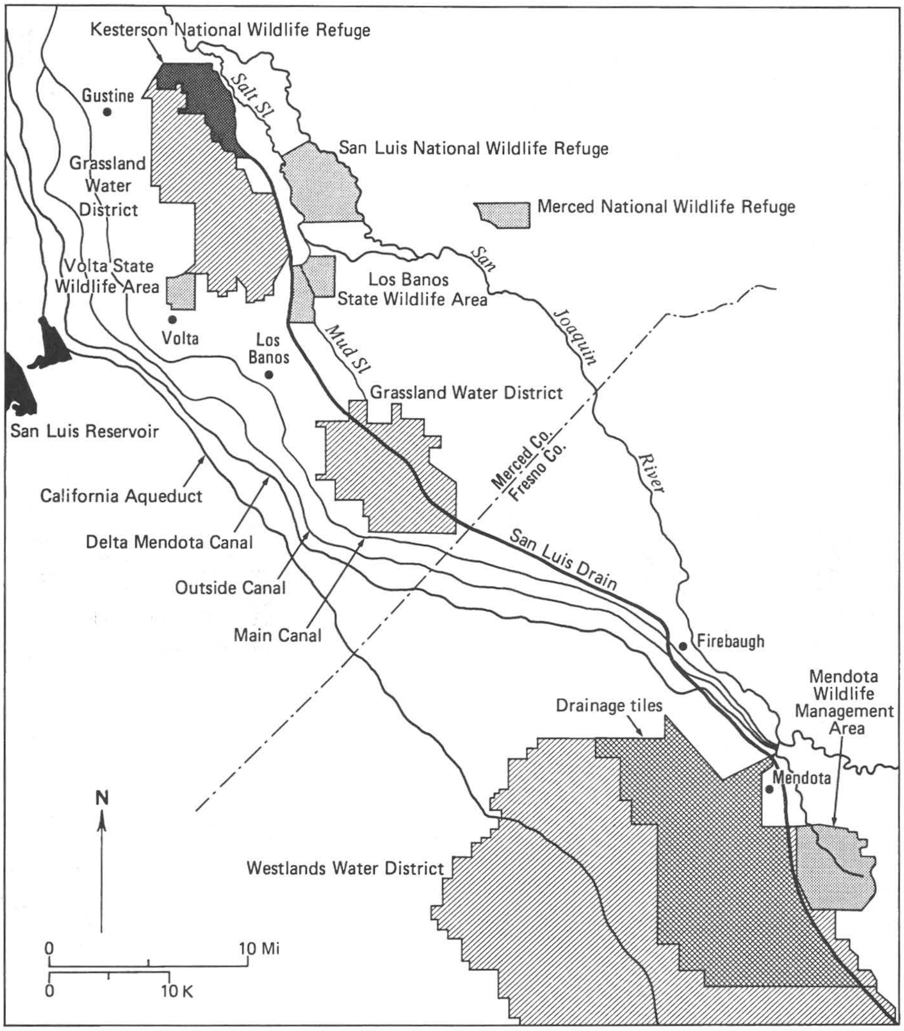

Figure 26.2. Main water distribution and drainage systems and wetlands in the study area, western San Joaquin Valley, Calif. (see figure 26.1 for location).

Presser and Barnes, 1984, 1985; Neil, 1986). Some of the specific findings follow (fig. 26.6).

1. Selenium concentrations ranged from 140 to 1,400 parts per billion (ppb) in irrigation drainage water entering the San Luis Drain.
2. Selenium concentrations were approximately 300 ppb in water flowing into Kesterson Reservoir from the San Luis Drain.
3. The selenium concentration in pond 2 of Kesterson Reservoir (the inflow point from the San Luis Drain) was 350 ppb.
4. Selenium concentrations in Kesterson pond 11 (farthest from the inflow from the San Luis Drain) were 14 ppb in August 1983 and 60 ppb in December 1983; this increase indicates uptake of selenium by aquatic organisms and sediments in Kesterson Reservoir.
5. Selenium concentrations as high as 4,200 ppb were observed in water from a drain below irrigated fields southeast of Oro Loma.
6. Inflow to Grassland Water District via Agatha Canal and Camp 13 Ditch had selenium concentrations ranging from 45 to 65 ppb.
7. Irrigation supply and surface-return waters and waters of Volta State Wildlife Area (which does not receive drain water) had selenium concentrations ranging from less than 2 to 10 ppb.
8. Detectable concentrations of selenium (1 ppb or greater) were found in the shallow ground water throughout the San Luis Drain Service Area. South of Los Banos, selenium concentrations generally were greater than 10 ppb. Selenium concentrations were highest in the vicinity of the Panoche fan where many

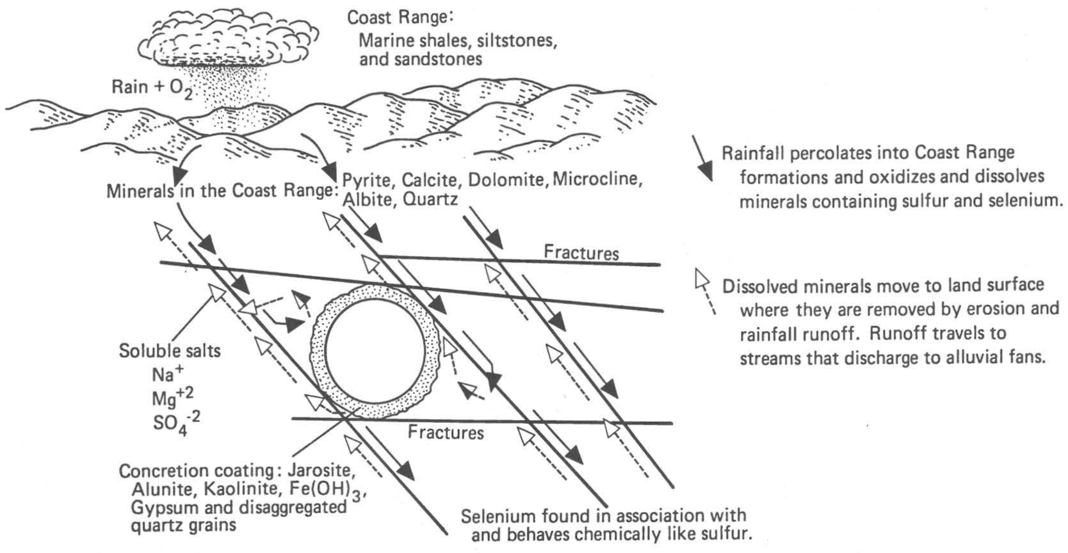

Figure 26.3. Conceptual model of sulfur and selenium mobilization and transport.

sites had concentrations greater than 500 ppb, the highest being 3,800 ppb. Some sites near Five Points in the Cantua Creek fan had selenium concentrations between 100 and 500 ppb. Only selenium, chromium, boron, and mercury were detected at concentrations approaching or exceeding recommended guidelines for the protection of freshwater aquatic life or agricultural crops.

9. Four of 63 wells sampled that withdraw water from the regional aquifer had selenium concentrations that exceeded 10 ppb, the U.S. Environmental Protection Agency's drinking-water standard. Two of 39 domestic wells had selenium concentrations of 11 and 13 ppb. Two of 11 irrigations and agricultural wells had selenium concentrations of 55 and 120 ppb.
10. Most of the shallow ground water in the San Luis Drain Service Area is alkaline and slightly to highly saline. These conditions are important, because selenium is very soluble when it is in an oxygenated alkaline environment, and under these conditions, it is very mobile in the aquifer and surface-water system. Thus, selenium can be easily transported from soils in the western San Joaquin Valley to subsurface tile drains, the San Luis Drain, and Kesterson Reservoir.

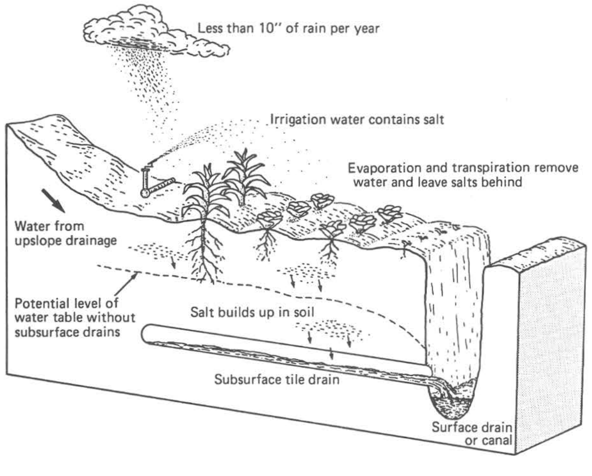

Figure 26.4. Climate, irrigation, and drainage in the western San Joaquin Valley, Calif.

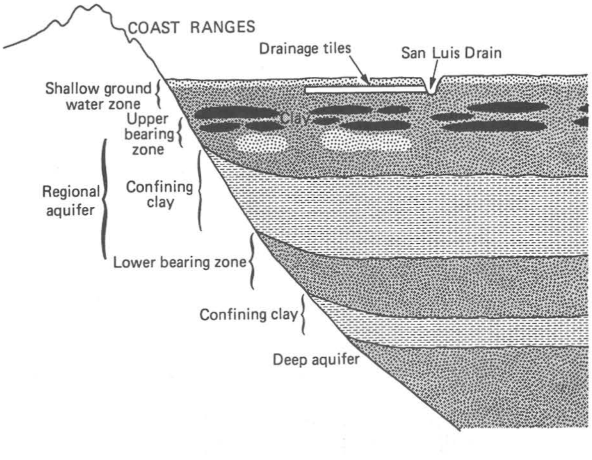

Figure 26.5. Cross-sectional sketch of western San Joaquin Valley, Calif., showing location of clay layers and major aquifers.

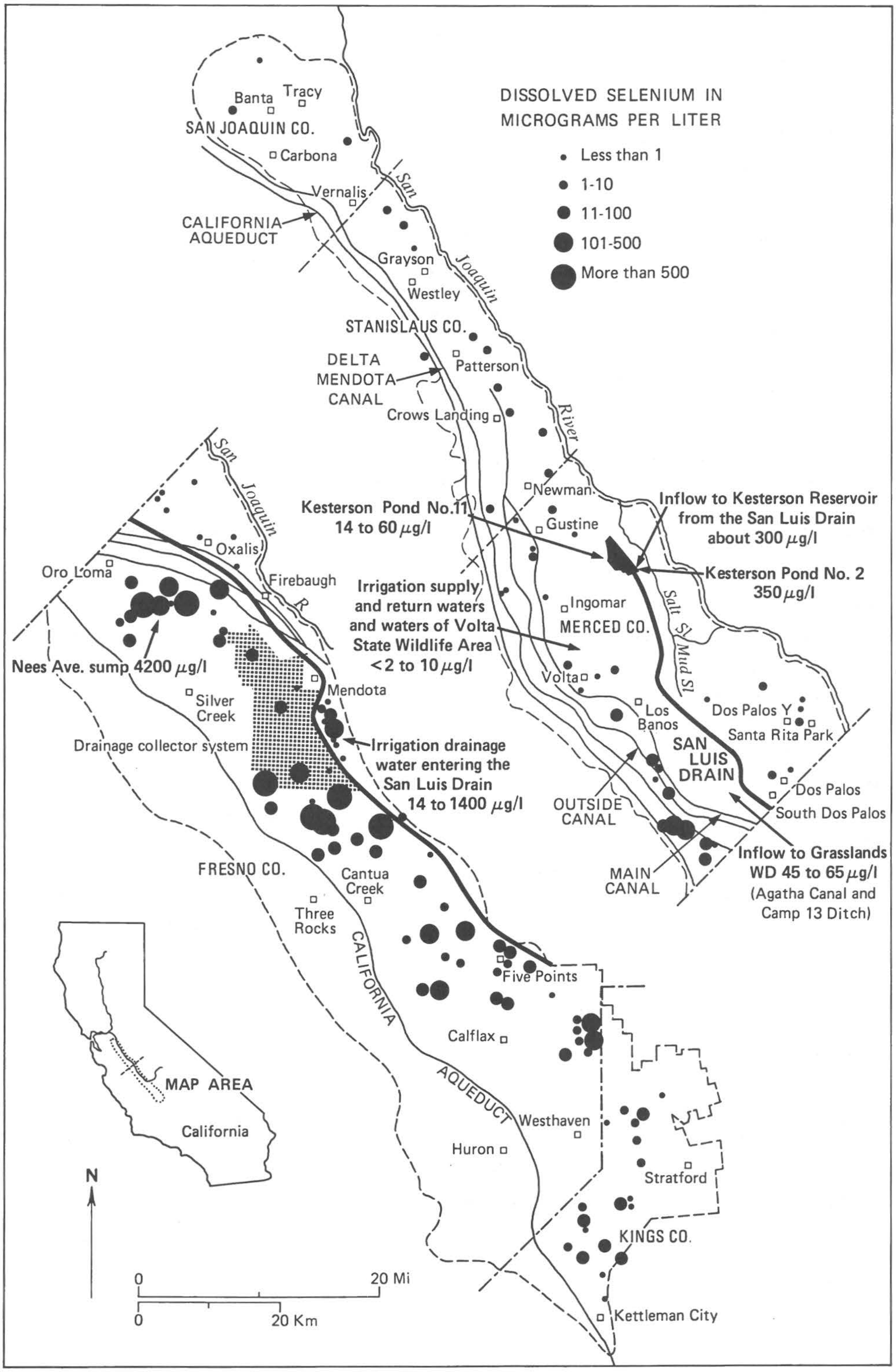

Figure 26.6. Selenium concentrations in surface and ground water of the western San Joaquin Valley from Tracy to Kettleman City, Calif.

11. The dominant water type is sodium sulfate, the predominant soluble salt in the bedrock of the Coast Ranges (fig. 26.3). This characteristic shows that waters in the western San Joaquin Valley were derived from runoff from the Coast Ranges. Thus, if the ultimate source of selenium is to be understood, geochemical studies are needed of the minerals and waters of the Coast Ranges, as well as such studies in the valley.
12. The USGS is doing a study of trace elements in Suisun Bay (Luoma and others, 1984). This study was started in 1983. Results show that sediments in Suisun Bay were typical of those in San Francisco Bay—coarse-grained sands to fine silt-clay enriched in manganese and iron. Sediment samples have been analyzed for silver, lead, copper, zinc, iron, manganese, and cadmium. Clams have been analyzed for silver, copper, zinc, and cadmium. Clam-tissue concentrations of silver and zinc are similar to those found in clams from pristine areas. Sediment and clams collected in 1984 and subsequent years will also be analyzed for selenium, mercury, and arsenic.

CONTINUING USGS STUDIES

Studies are continuing to:

1. Confirm the source of selenium.
2. Better define the distribution of selenium and other constituents in the waters and soils of the western San Joaquin Valley.
3. Determine the processes controlling the mobility, transport, and fate of selenium and other constituents in the waters, sediments, and soils of the western San Joaquin Valley.
4. Describe the geology and movement of water and solutes in the western San Joaquin Valley.
5. Assess the occurrence and transport of selenium and other constituents in the San Joaquin River.
6. Determine concentrations of trace elements, including selenium in the sediments and in selected aquatic organisms of the San Francisco Bay and delta.

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27. A Potential Source Area for Selenium and Mercury in Agricultural Drainage Water at Kesterson Reservoir, San Joaquin Valley, California

By Ronald R. Tidball, R.C. Severson, James M. McNeal, *and* Stephen A. Wilson

Abstract

Agricultural drainage water collected from the San Luis Unit of the Federal Central Valley Project irrigation development on the west side of the San Joaquin Valley, Calif., has been channeled through the San Luis Drain canal into an evaporation reservoir in the Kesterson National Wildlife Refuge. The water, plants, sediments, and aquatic life contain high levels of selenium, which is believed to be responsible for a high incidence of mortality among nesting birds in the area (U.S. Bureau of Reclamation, 1984). Analyses of several hundred soil samples from throughout the San Joaquin Valley and the San Luis Drain Service Area on the west side of the valley show there are two major anomalous areas for selenium—the Panoche-Cantua Creek alluvial fans in the service area in western Fresno County and the Antelope Hills in western Kern County. There is one major anomaly for mercury—the Panoche-Cantua Creek area. Soil samples from the service area indicate that the selenium source area is in the vicinity of Monocline Ridge on a mudflow deposit between Panoche fan and Cantua fan. The higher mercury values on both Panoche Creek and Cantua Creek fans indicate alluvial dispersion trains that originate in the New Idria mercury district about 20 miles upstream.

INTRODUCTION

Surface irrigation water was first imported into the San Joaquin Valley from the north when the Delta-Mendota Canal commenced operation in 1951 under the Federal Central Valley Project. The San Luis Unit, the most recent area to be developed on the west side of the San Joaquin Valley in western Fresno, Merced, and Kings Counties, Calif., first received water through the Delta-Mendota and the San Luis canals in 1967 (San Joaquin Valley Interagency Drainage Program, 1979). Soils in the area have long been notable for adverse salinity conditions and a high water table especially near the valley trough (Mendenhall and others, 1916). To mitigate these conditions, the San Luis Drain, a concrete-lined canal that borders the lower edge of the San Luis Unit (San Luis Drain Service Area; fig. 27.1), hereafter referred to as the service area, was constructed between 1968 and 1975. The canal extends for 82 miles from a point just east of Five Points in Fresno County, Calif., to Kesterson National Wildlife Refuge in Merced County near Gustine, Calif. Kesterson Reservoir was orig-

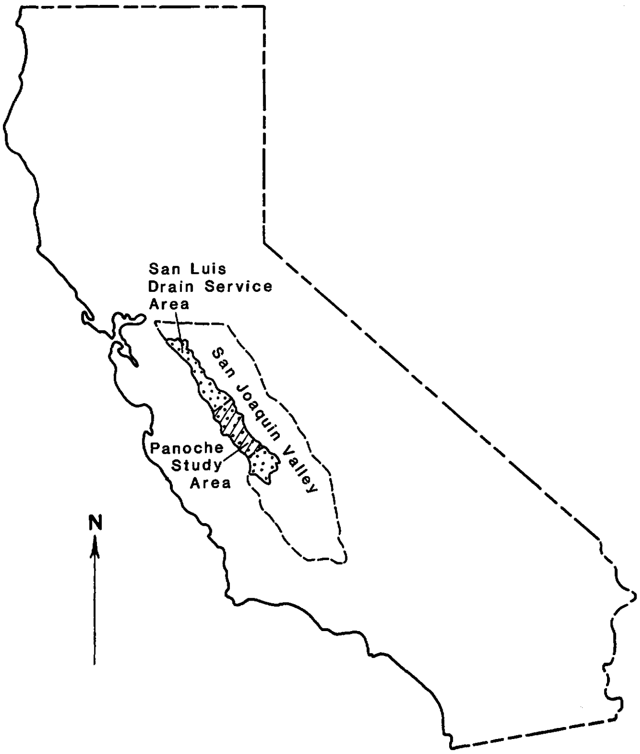

Figure 27.1. Map of California showing location of study area—San Luis Drain Service Area, Panoche fan, and San Joaquin Valley, Calif.

inally intended to be a regulating reservoir for the canal, which was to extend to the San Joaquin-Sacramento River delta for discharge. However, the canal was never finished, and Kesterson Reservoir, which is a series of 12 ponds covering 1,280 acres, became the temporary terminus. Salts have accumulated in the ponds because the only outlet is through evaporation or seepage.

The purpose of this study was to discover the geologic source of the trace elements that are causing toxic conditions at Kesterson. We determine that source by identifying, with an areal survey of element distribution in soils, those localities having geochemical anomalies as compared to a background level. This report shows the distribution of selenium in soils and its potential geologic source. We also include the distribution of mercury because a world-class mercury mineralization district is located in the Diablo Range adjacent to the service area.

METHODS

Field and laboratory methods have been described by Tidball and others (1989). Data handling has been described by Tidball and others (1986). In 1983, soils were sampled throughout the San Joaquin Valley at 297 sites about 10 km apart. These valley samples represent a composite sample of the 0- to 12-inch (0- to 30-cm) depth of the soil. In 1985, soils were also sampled on the Panoche-Cantua Creek fan area at 721 sites 1 mile apart. The Panoche samples represent a composite sample of the 66- to 72-inch (168- to 183-cm) depth of the soil. The clay fraction (less-than-2-mm size fraction) of all samples was analyzed for total concentrations of selenium by hydride generation and atomic-absorption spectrophotometry (Briggs and Crock, 1986) and for total mercury by cold-vapor atomic-absorption spectrophotometry (Kennedy and Crock, 1987).

The observed data points were used as the basis for estimating a grid of points by kriging (Tidball and others, 1986). The grid for the valley soils, which were collected at about 10-km intervals, was estimated at 2-km intervals. The grid for the Panoche samples, which were collected at 1-mile intervals, was estimated at 0.5-km intervals. A gray-scale display was compiled from the gridded data.

RESULTS

The distribution map of selenium in the valley (fig. 27.2) shows that above-average selenium values are found on the west side of the valley and below-average values on the east side. Thus the granitic terrane of the Sierra Nevada, which provided the valley-fill sediments for the eastern part of the valley, is an insignificant source of selenium. The overall pattern indicates the presence of a broad-scale but moderate-level source of selenium on the west side within or at the edge of the Diablo Range. Once the overall perspective is available, it is readily apparent that certain localities stand out as anomalies. Those localities include the Panoche-Cantua Creek fans in the service area, the Antelope Hills in western Kern County, and Maricopa Flat in southwestern Kern County. In all three areas, the anomalies border on sedimentary rocks that range from marine units of Cretaceous age through nonmarine units of Quaternary age. The map showing mercury distribution in the valley soils (fig. 27.3) indicates that a significant mercury anomaly is located in the Panoche-Cantua Creek area. Three less significant anomalies are found along the west and south sides of the valley.

The detailed map of selenium in Panoche samples (fig. 27.4) shows that selenium is not associated with either of the two larger present-day alluvial fans of Panoche and Cantua Creeks but is on an interfan area bordering Monocline Ridge. The interfan area is likely to be composed of coalescing alluvial fans that are overlain by mudflow deposits near the foothills. The mudflows were probably derived from sedimentary rocks of one or more of the adjacent formations—the nonmarine Tulare Formation, the marine Etchegoin Formation, the marine Kreyenhagen Shale, and perhaps other formations further back into the foothills.

The map showing mercury distribution in the Panoche samples (fig. 27.5) indicates that mercury is associated with the alluvial sediments of both Panoche Creek and Cantua Creek. A major mercury mineralization district is located along the New Idria fault that flanks a large intrusive body of ultrabasic rocks near the town of Idria. The New Idria mine was the second largest producer of mercury in North America between 1858 and 1972. Other smaller mines are scattered throughout the district. Streams that drain the north, east, and south sides of the district all have outwash fans in the valley. Panoche Creek fan, which drains the north side of the district, exhibits the most prominent dispersion train for mercury, followed by the Cantua Creek fan, which drains the east side.

DISCUSSION

The location of the source area of selenium is clearly in or near the San Luis Drain Service Area. The ultimate host material for selenium is unknown at this time, but for the present the soil and the ground water are a repository for selenium. Undoubtedly, deeper sediments also contain selenium. A source area in the vicinity of Monocline Ridge would suggest that one or more sedimentary-rock strata are the host rocks. Based on a common type of occurrence of selenium in other parts of the west, the host may be a shale of marine origin. Lakin and Byers (1941) found 28 parts per million (ppm) selenium in the marine Moreno Shale in the

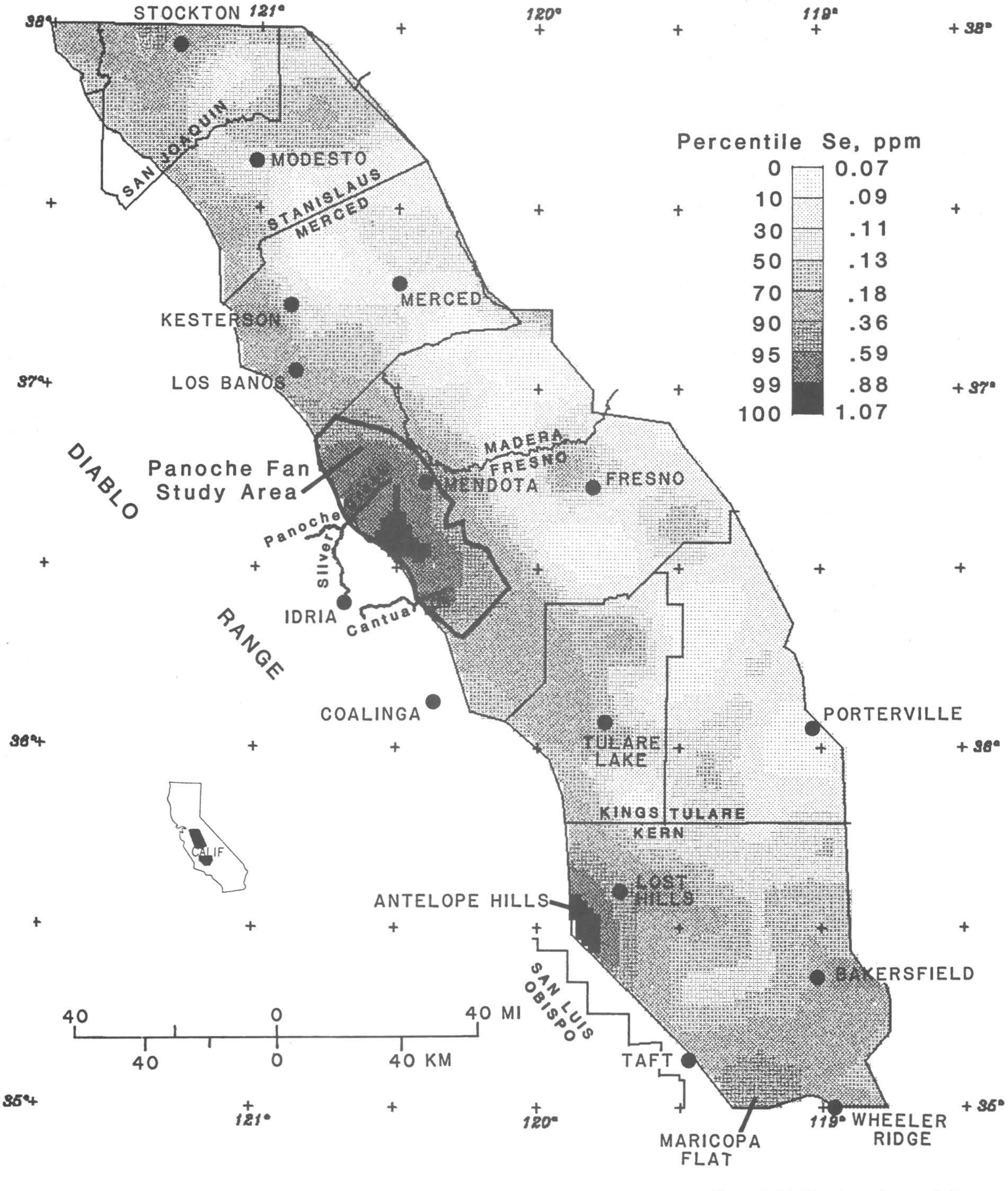

Figure 27.2. Distribution of selenium at 0- to 12-in. depth of soils in the San Joaquin Valley, Calif. Shades of gray delineate percentiles of the distribution of median values for each 2-km cell. ppm, parts per million.

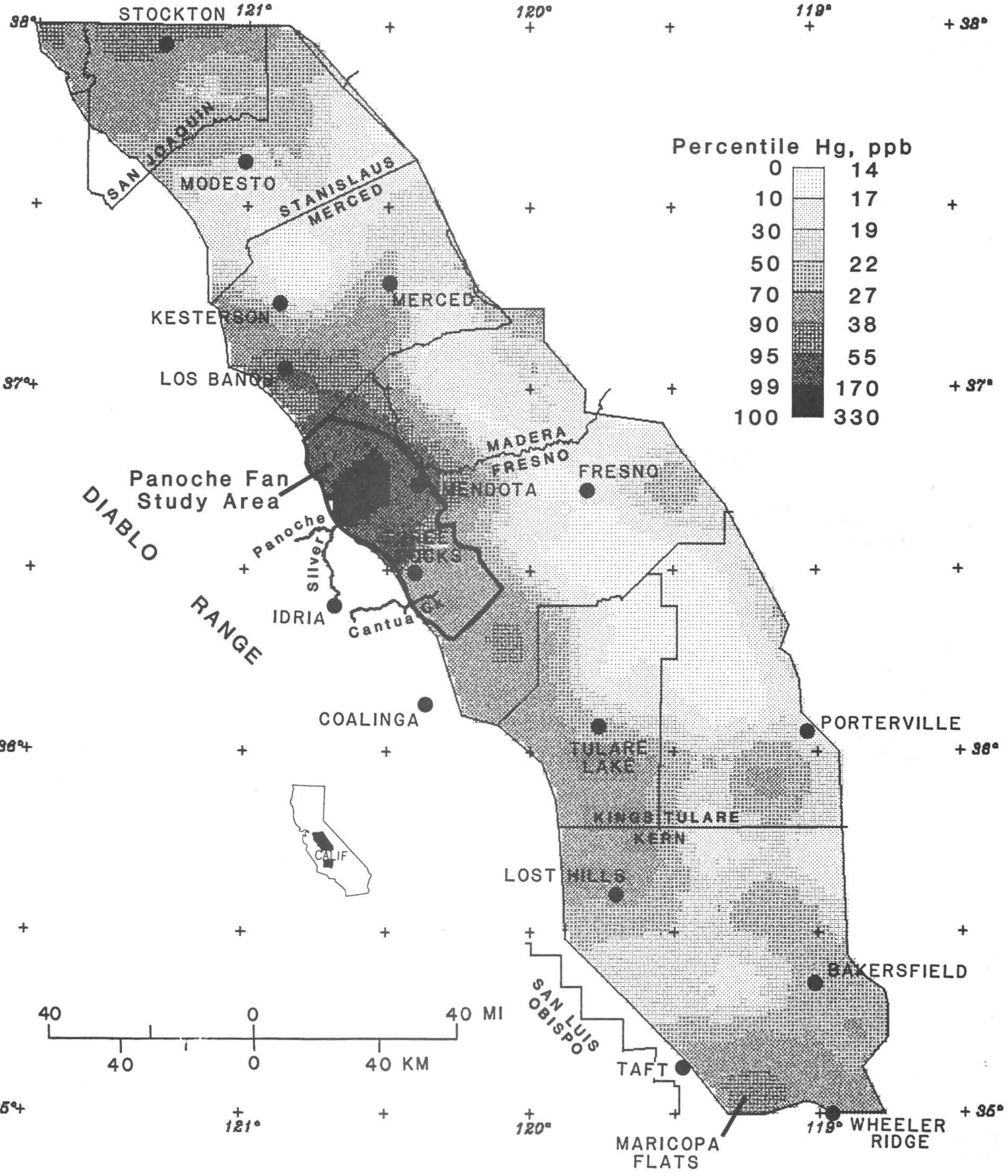

Figure 27.3. Distribution of mercury at 0- to 12-in. depth of soils in the San Joaquin Valley, Calif. Shades of gray delineate percentiles of the distribution of median values for each 2-km cell. ppb, parts per billion.

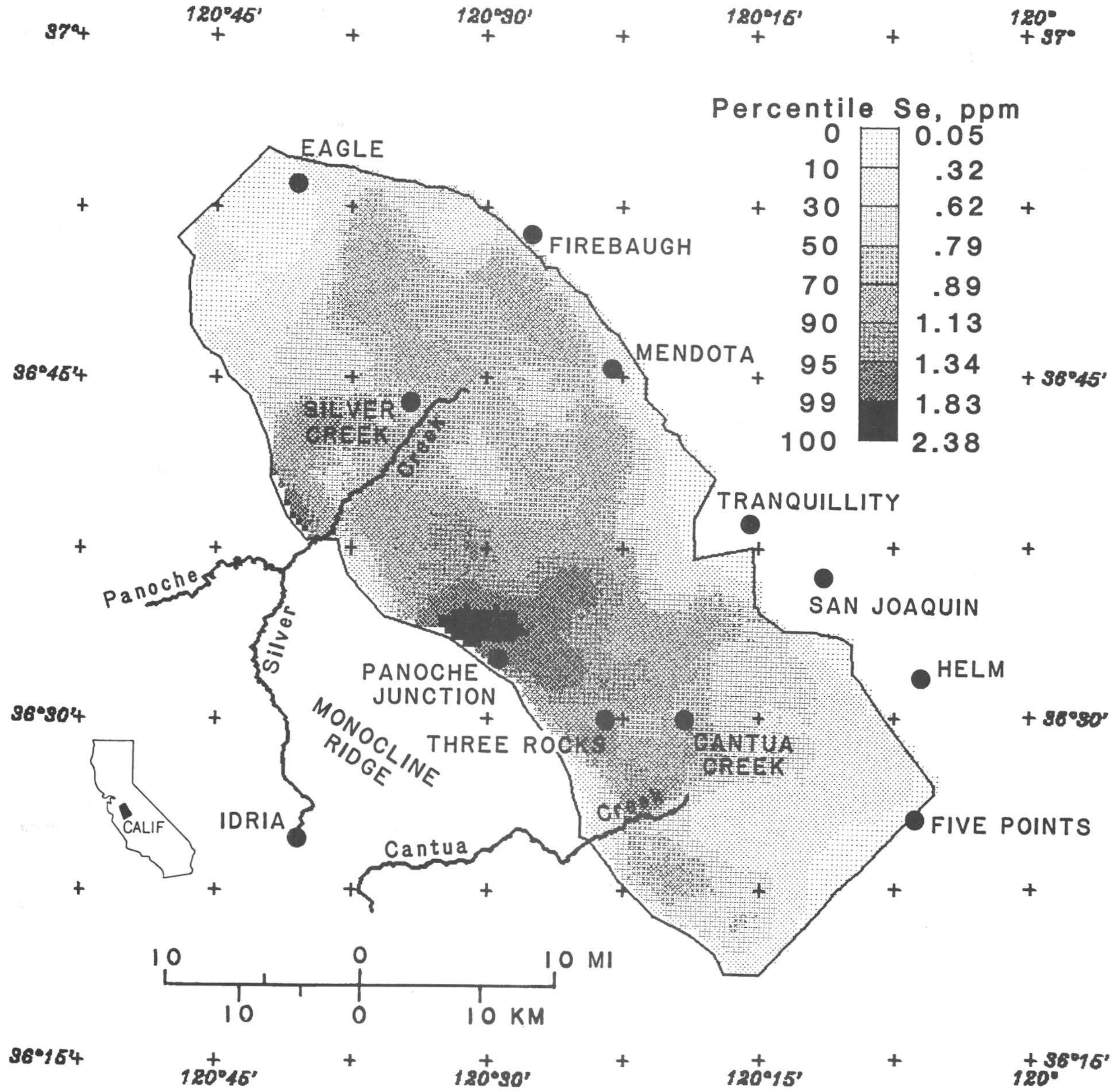

Figure 27.4. Distribution of selenium at 66- to 72-in. depth of soils in the Panoche-Cantua Creek fan area, San Luis Drain Service Area, Calif. Shades of gray delineate percentiles of the distribution of median values for each 2-km cell. ppm, parts per million.

Diablo Range about 65 miles northwest of Monocline Ridge. The proximity of the mercury mineralization district at New Idria, as well as hints of an association of selenium with other ultrabasic intrusives in the southern part of the valley, is either a remarkable coincidence, or it suggests that selenium and mercury were deposited by a common process. A possible explanation is that, even though selenium may be hosted in a sedimentary unit, the ultimate source of selenium may be the hydrothermal solutions that were associated with these intrusives or with nearby faults.

SUMMARY

It appears that selenium, which is bioaccumulating in plants and fauna in the Kesterson Reservoir area, was transported to the reservoir with other soluble salts in agricultural drainage water from saline soils and ground waters located in the San Luis Drain Service Area in western Fresno County. The geomorphic setting of the service area is the Panoche-Cantua Creek fans, which abut down-dipping sedimentary rock strata at the mountain front.

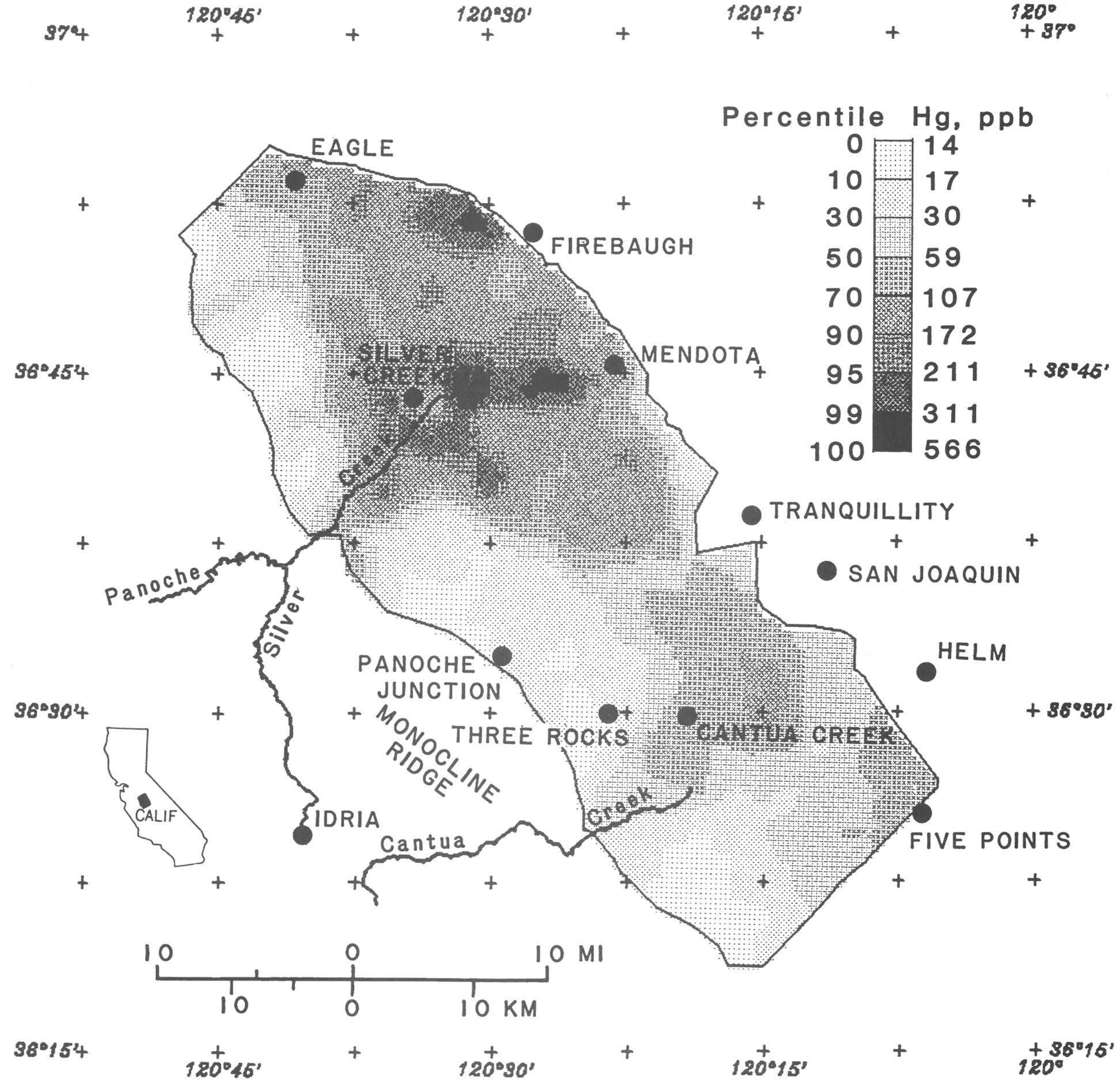

Figure 27.5. Distribution of mercury at 66- to 72-in. depth of soils in the Panoche-Cantua Creek fan area, San Luis Drain Service Area, Calif. Shades of gray delineate percentiles of the distribution of median values for each 2-km cell. ppb, parts per billion.

A major source of selenium is in the vicinity of Monocline Ridge and may result from local mudflow deposits rather than alluvium from within the interior of the Diablo Range. Although the present repository of selenium is in the soils, sediments, ground water, and perhaps nearby sedimentary rock units, the ultimate source of selenium may be associated with the same geological processes that were responsible for the major mercury mineralization zone at New Idria about 20 miles southwest of the service area.

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28. Geoelectrical Studies on the Panoche Fan Area of the San Joaquin Valley, California

By Robert J. Bisdorf

INTRODUCTION

In 1985, the U.S. Geological Survey made 82 Schlumberger direct current resistivity soundings and ran 18 electromagnetic profiles in the Panoche fan area of California. The Panoche fan is located in the central section of the San Joaquin Valley, west of Mendota, Calif. (fig. 28.1). The geoelectrical studies were part of a larger effort to study sources of selenium and selenium contamination of ground water. Deverel and others (1984) reported high levels of selenium in shallow ground-water samples at the edges of the fan. Of particular hydrologic interest is the presence or absence of a clay layer, usually in the upper 100 m, that creates a perched aquifer in parts of the fan. It is possible that the clay layer contributes to high selenium concentrations by not allowing irrigation waters to percolate downward. The geoelectrical studies were designed to detect the presence or absence of this clay layer.

GEOELECTRICAL SURVEY

Schlumberger soundings were chosen as the main geophysical tool because of their long history of successful application in ground-water studies. The Geonics EM–34, an electromagnetic geophysical tool, was used at 18 sites to evaluate its usefulness for further studies. Only the Schlumberger sounding data and interpretations are presented in this report. Figure 28.1 shows the location and identifying number of the 82 Schlumberger soundings.

Schlumberger sounding is a direct-current resistivity technique that involves injecting current into the ground through two metal electrodes (A and B) and measuring the electric field with two other electrodes (M and N) centrally located between the A and B electrodes. An apparent resistivity is calculated by using a formula that relates the measurement made with the M and N electrodes, the amount of current injected into the ground, and the distances between the A–B and M–N electrode pairs (Zohdy and others, 1974). The A and B electrodes are moved successively to larger separations to probe deeper. Figure 28.2 shows two typical Schlumberger sounding curves, Panoche 50 and Panoche 56, whose locations are indicated by the asterisks on figure 28.1. Sounding Panoche 50 indicates the presence of higher resistivity material than does sounding Panoche 56. Schlumberger soundings are usually interpreted as a series of horizontal layers of varied resistivities and thicknesses. The Panoche fan sounding data were interpreted by using a program by Zohdy (1974), modified to run on a desktop computer using a more precise set of linear filter coefficients developed by O'Neill (1975).

RESISTIVITY MAPS

To show the areal distribution of resistivity, maps of interpreted resistivity at a particular depth were generated by determining, for each sounding, the interpreted resistivity at that depth. These data and the *x-y* coordinates of each sounding were put into a gridding program (Webring, 1981), and the output was contoured. Maps of interpreted resistivity at depths of 5, 10, and 20 m are presented as figures 28.3, 28.4, and 28.5, respectively. Each map can be thought of as looking at a slice of the Earth's resistivity distribution at that depth.

In the forthcoming discussion of the interpreted resistivity maps, the following assumptions and interpretive criteria are used. Resistivities greater than 20 ohm-m represent relatively coarse-grained material (sand-gravel) and as such will probably exhibit high porosity and (or) permeability. Resistivities less than 7 ohm-m represent relatively fine-grained materials (clay). The lower the resistivity, the larger the proportion of clay. These criteria assume that the ground-water quality is about the same over the area of interest; this probably is a valid assumption, especially in the upper 50 m, because the major source of shallow ground water is irrigation water from the California aqueduct. If this assumption is not valid, then the resistivities may be ground-water salinity indicators as well as, or instead of, lithologic indicators. The results of water sampling may validate this assumption.

Soundings Panoche 50 and 56, as shown in figure 28.2, indicate the response of Schlumberger soundings to

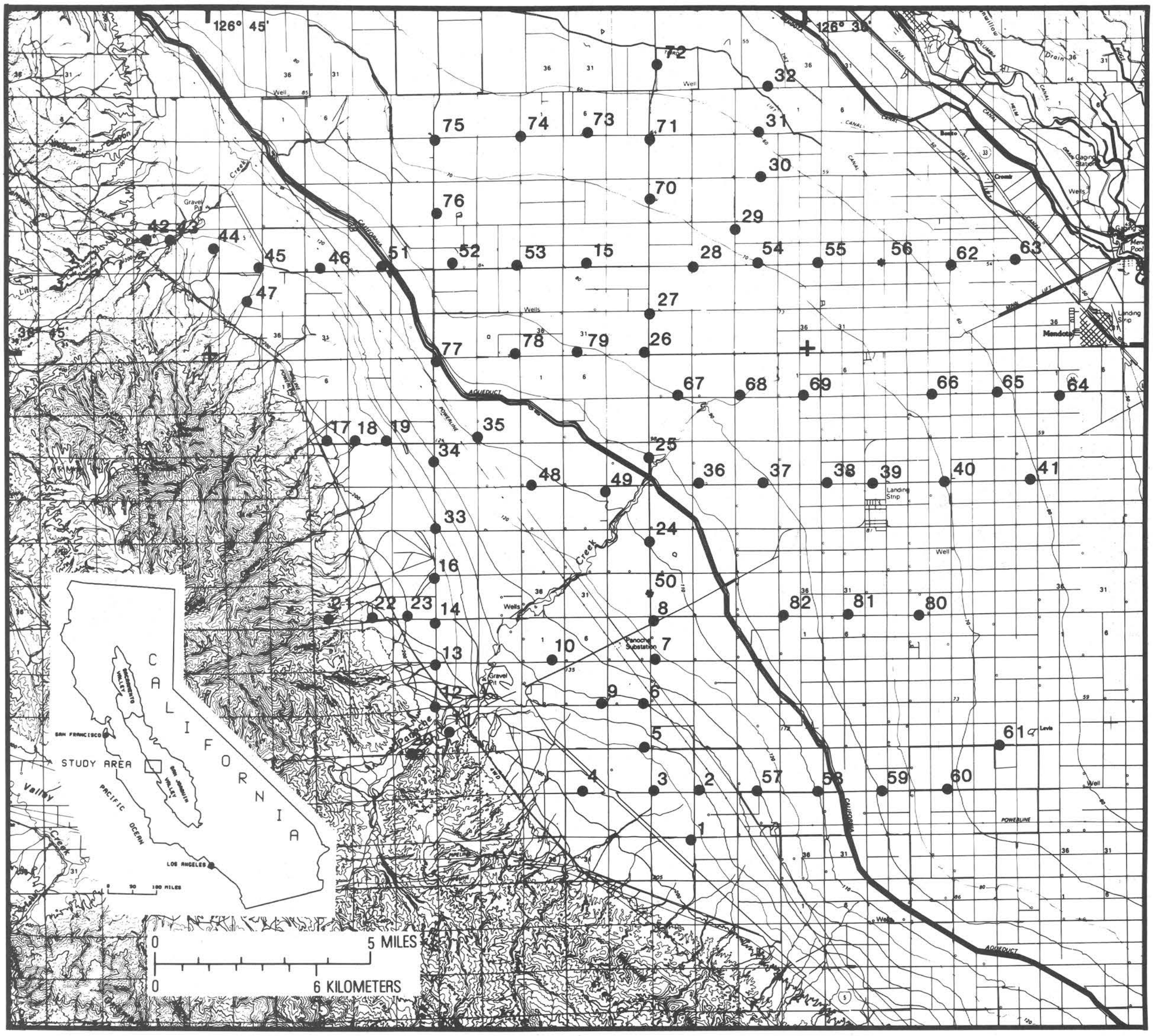
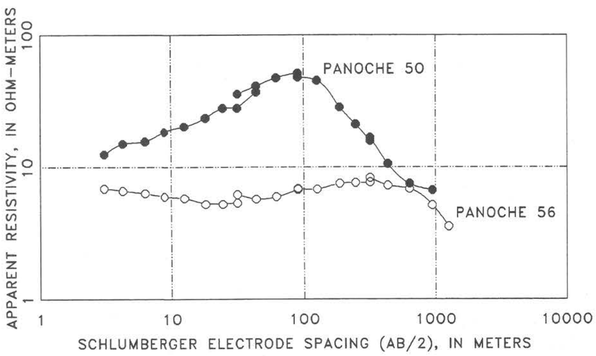


Figure 28.1. Location and identifying number of the Schlumberger soundings, Panoche fan area, California. Asterisks indicate locations of soundings whose curves are shown in figure 28.2.



◀ **Figure 28.2.** Two typical Schlumberger sounding curves, Panoche fan area, California. Sounding Panoche 50 shows the response to higher resistivity material, and sounding Panoche 56 shows the response to the lower resistivity material. The locations of these soundings are highlighted on figure 28.1 with asterisks.

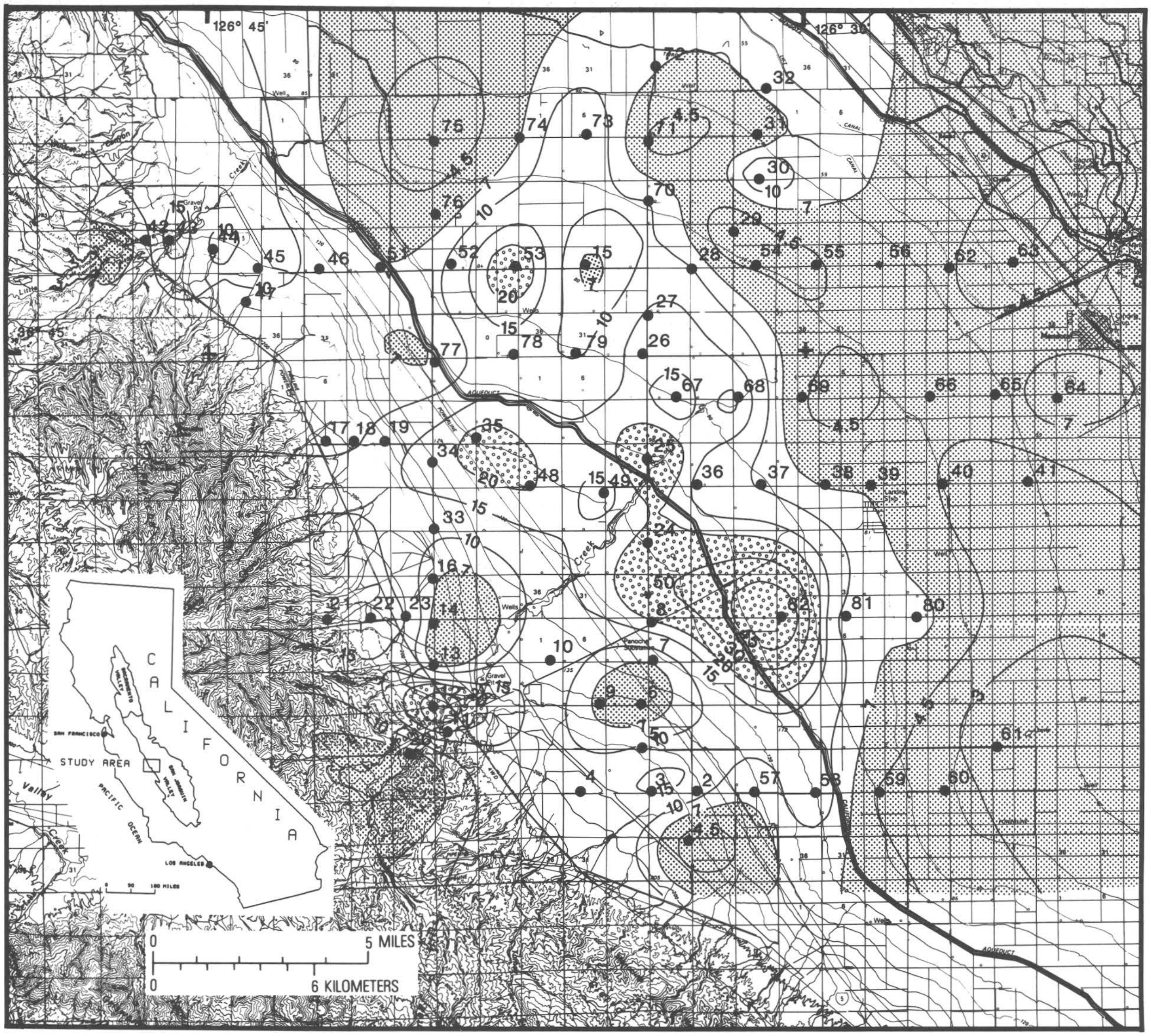


Figure 28.3. Contour map of interpreted resistivity at a depth of 5 m, Panoche fan area, California. The dot pattern indicates areas of resistivities of greater than 20 ohm-m. The stipple pattern indicates areas of resistivities of less than 7 ohm-m. Contour values are in ohm-m.

the presence of coarse- and fine-grained material. Sounding Panoche 50 is located in an area having resistivities greater than 20 ohm-m in the upper 80 m; these values indicate the presence of relatively coarse-grained material. Sounding Panoche 56 is located on the margin of the fan where the resistivities are less than 7 ohm-m in the upper 80 m; these values indicate the presence of relatively fine-grained material.

Figure 28.3 shows the resistivity map for a 5-m depth. It is interesting to note that the lower center of the map, roughly corresponding to the center of the fan, has a zone of resistivities of greater than 20 ohm-m and that the edges of the map show resistivities of less than 7 ohm-m. This contrast indicates that the center of the fan is composed of relatively coarse-grained material and that the edges of the fan have a high percentage of clay. The parts of the map that show resistivities between 7 and 20 ohm-m are in an intermediate zone where the composition is probably mixed. Other information will be needed to classify these areas.

Figure 28.4 shows the resistivity map for a 10-m depth. As in the map for a 5-m depth, this map shows that the center of the fan is composed of mostly coarse-grained material and the edges are composed of mostly clay. The high-resistivity zone in the center of the fan extends southwest toward the mouth of Panoche Creek and indicates

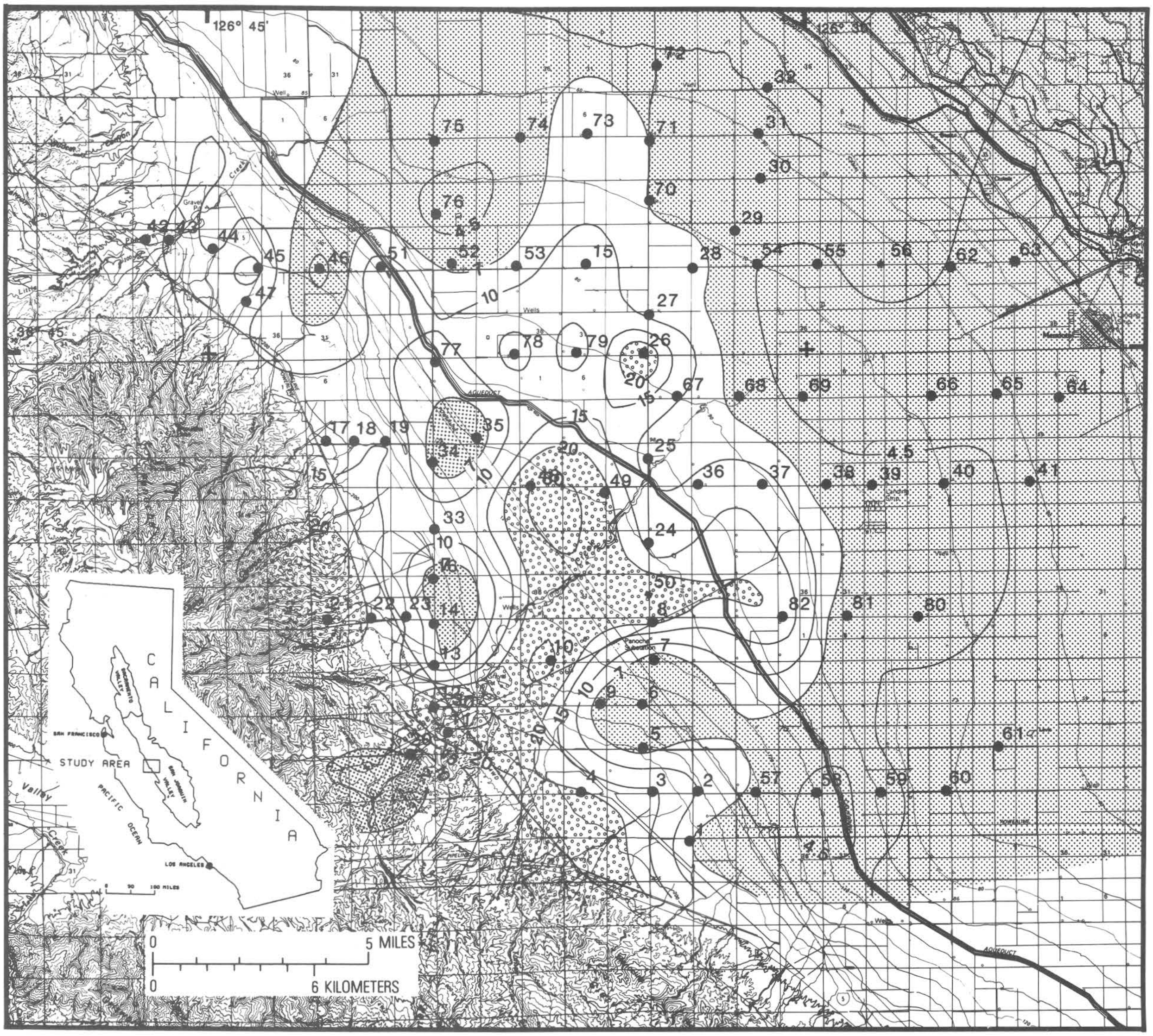


Figure 28.4. Contour map of interpreted resistivity at a depth of 10 m, Panoche fan area, California. The dot pattern indicates areas of resistivities of greater than 20 ohm-m. The stipple pattern indicates areas of resistivities of less than 7 ohm-m. Contour values are in ohm-m.

that the coarse-grained material may be related to the Panoche Creek drainage.

Figure 28.5 shows the resistivity map for a 20-m depth. Again the center of the fan shows high resistivities and indicates mostly coarse-grained material. The edges of the fan seem to be composed of clay, and it seems that the northern edge of the fan is somewhat lower in resistivity at this depth than at the other depths; this value indicates a higher clay content. The intermediate resistivities are less prevalent at this depth, and as the high-resistivity zone did not increase in area, the low-resistivity zone has gotten larger. This trend continues on the maps of depths greater than 20 m, which are not presented here.

CONCLUSIONS

Schlumberger soundings appear to map the presence or absence of clays, at least in a gross sense, in the Panoche fan area. In general, the center of the fan appears to have much less clay than the edges. In addition, the coarse-grained central fan area appears to be related to the Panoche Creek drainage. This makes sense as the Panoche Creek probably transported whatever coarse material there was. Resistivity maps not presented here indicate that the coarse-grained material appears to disappear at depths greater than 200 m. This disappearance may be real or higher salinity ground water may be masking the presence of the coarse-

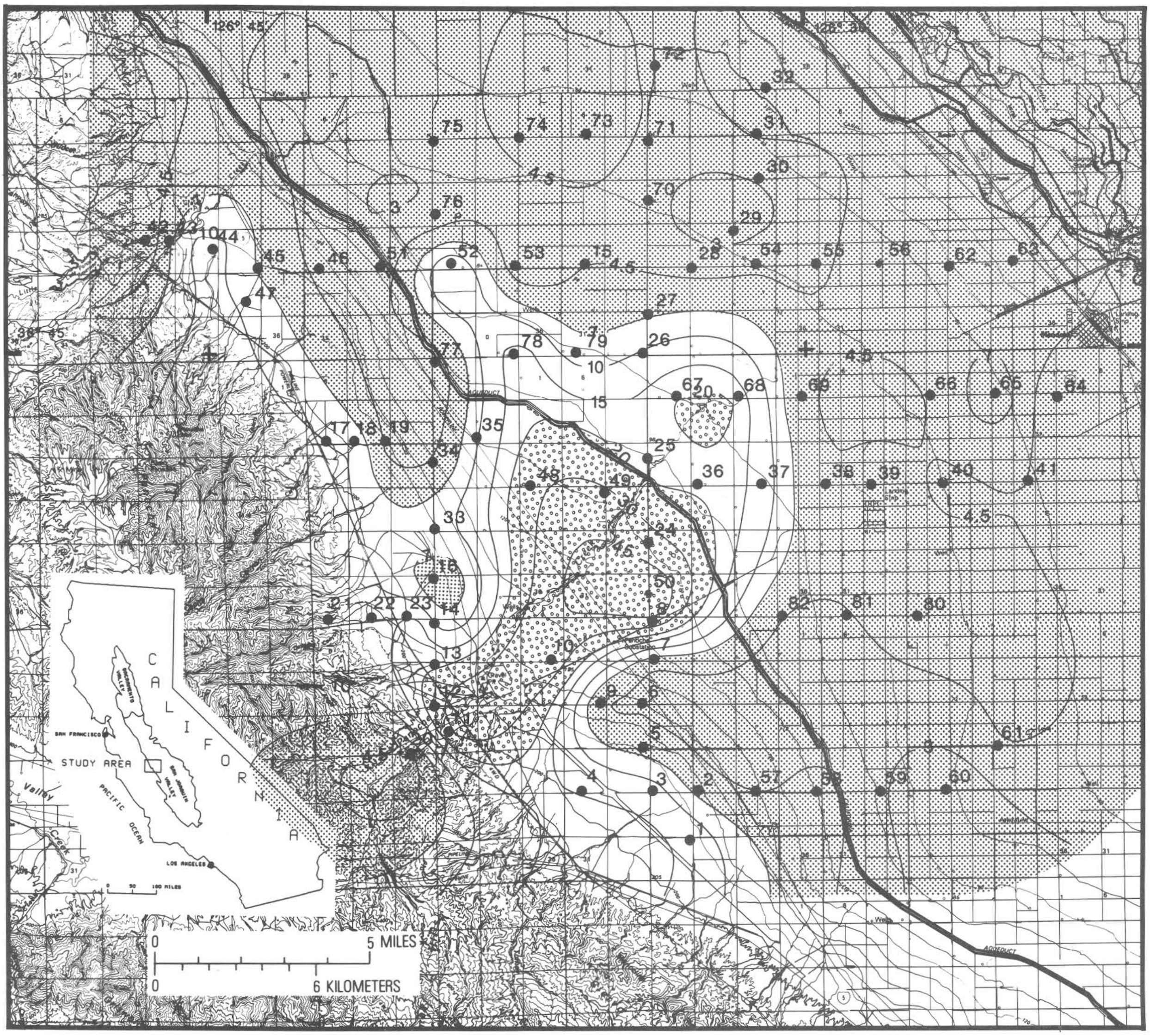


Figure 28.5. Contour map of interpreted resistivity at a depth of 20 m, Panoche fan area, California. The dot pattern indicates areas of resistivities of greater than 20 ohm-m. The stipple pattern indicates resistivities of less than 7 ohm-m. Contour values are in ohm-m.

grained material. The assumption of uniform ground-water quality may not be valid at depths greater than 50 m.

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29. Initial Shallow Seismic Tests in the Panoche Fan Area, Fresno County, California

By Wilfred P. Hasbrouck

INTRODUCTION

During April 1985, the U.S. Geological Survey conducted seismic tests at four widely spaced sites on the Panoche fan, Fresno County, Calif., to develop a relatively inexpensive, high-resolution, reflection method that can be used to map a clay layer at a depth of less than 100 m. Both longitudinal- (P-) and shear- (S-) wave procedures were investigated. The primary source of seismic energy was a 9.1-kg hammer struck vertically against a 15-cm^2 aluminum plate or horizontally against a steel fixture pinned to the ground with eight spikes. Seismic arrivals were detected by 40-Hz seismometers whose outputs were linked through an interface unit to a 12-channel, signal-enhancement engineering seismograph and digitally stored on magnetic tape. All data processing was done on a desktop computer.

SPOT-TEST RESULTS FROM SEISMIC SITE 1

Shear-wave reflections were detected on wave tests, and spot tests taken at seismic site 1 (NW corner, NE1/4 sec. 25, T.13 S., R.12 E.), near location 53 of Bisdorf's Schlumberger direct-current resistivity survey (Bisdorf, this volume, fig. 28.1). Three radial-source/radial-seismometer, shear-pair seismograms obtained along this line are shown in figure 29.1. Arrivals that have a convex alignment (dashed line) and are centered at 450 ms have the charac-

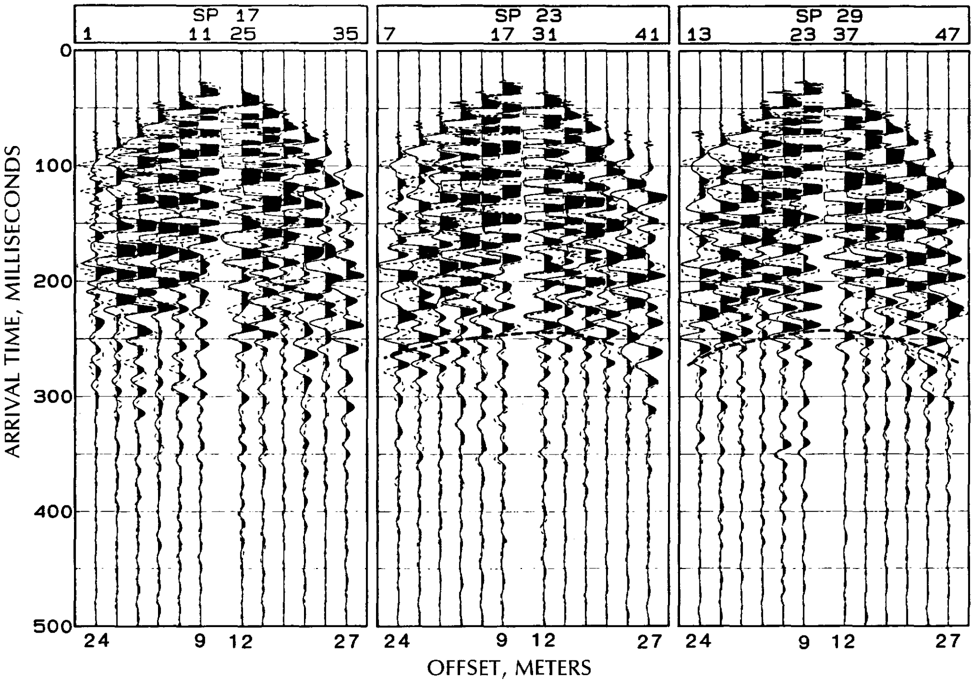

Figure 29.1. Three radial-source/radial-seismometer, shear-wave, spot-test seismograms from seismic site 1, Panoche fan area, California. The dominant arrival at about 450 ms (dashed line) has the characteristics of a seismic event reflected from a horizon at a depth of approximately 36 m. SP, shot point.

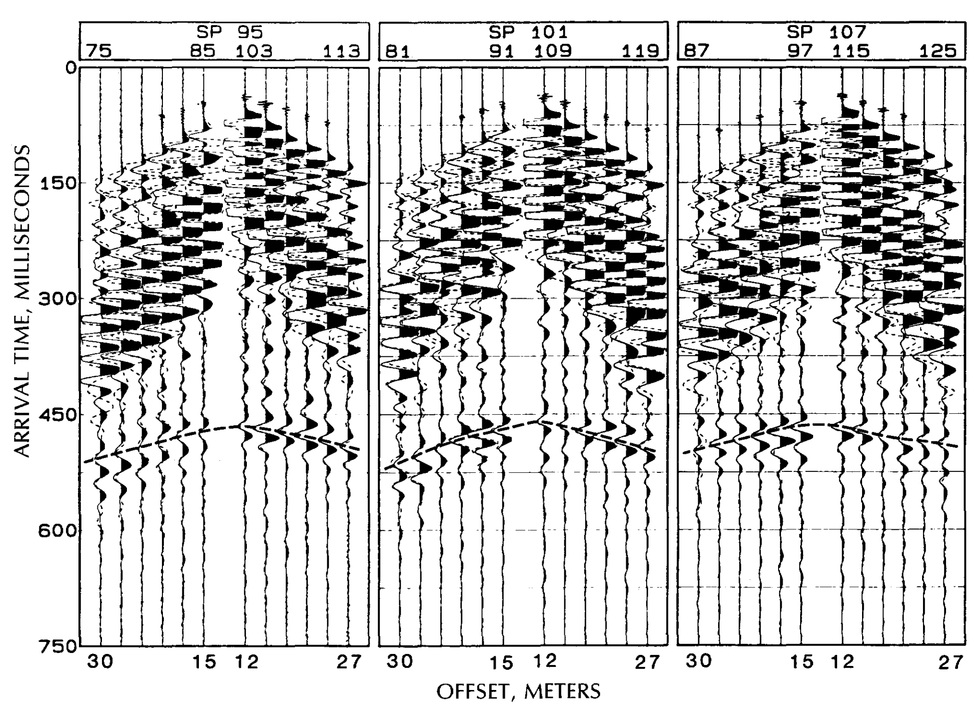

Figure 29.2. Three radial-source/radial-seismometer, shear-wave, spot-test seismograms from seismic site 3, Panoche fan area, California. Suggestions of a reflected event occur at 250 ms (dashed line), an estimated horizon depth of 20 m, on the record from shot point (SP) 29.

teristics of seismic reflections. Using a velocity of 160 m/s, obtained from analysis of a series of velocity panels, the computed depth of this seismic horizon is 36 m.

At electrical site 53, Bisdorf's soundings (personal commun.) indicate that the top of a low-resistivity layer of 4 ohm-m (a clay?) occurs at a depth of 12 m and the electrical section maintains a resistivity of less than 7 ohm-m to a depth of more than 1,000 m. No significant change in resistivity was observed at a depth of 36 m.

SPOT-TEST RESULTS FROM SEISMIC SITE 3

Shown on figure 29.2 are spot-test results obtained at seismic site 3, near location 68 of the electrical survey (Bisdorf, this volume, fig. 28.1), and 7.3 km east and 3.3 km south of seismic site 1. Spot-test responses at seismic sites 1 and 3 clearly are not the same, implying that the stratigraphic sections differ—as would be expected in a fan environment. Near-surface rocks at seismic site 3 have a higher velocity (as evidenced by less time for the first reflection arrivals), and the dominant reflection seen at about 450 ms at site 1 is not present. A suggestion of a reflection event at approximately 250 ms is shown by the dashed lines on the seismograms taken at shot points (SP's) 23 and 29.

At electrical site 68, Bisdorf's soundings (personal commun.) indicate that the top of a low-resistivity layer of 5 ohm-m (a clay?) occurs at a depth of 7.5 m and that an increase in resistivity to 19 ohm-m is found between 16.4 to 24.4 m, beyond which the electrical section exhibits resistivities ranging from 10 to 4 ohm-m. Clearly, seismic sites 1 and 3 are geophysically dissimilar.

SEISMIC SECTION AT SITE 1

To see if the high-quality reflection events obtained on spot tests at seismic site 1 persist laterally, a line of 112 shear-wave seismic records was taken and processed with a sixfold, common-midpoint procedure. From inspection of this seismic section, shown on figure 29.3, the near surface at site 1 appears to be composed of relatively flat, discontinuous beds and lenticular bodies. The lower reflection horizon (lower arrow on fig. 29.3) appears to carry across the section and exhibits gentle stepping down to the west (left side). The display of figure 29.3 is an unmigrated time section, not a depth section, and an increase in average velocity of less than 7 percent would be sufficient to reverse the apparent westward dip. In general, velocity increases with grain coarseness within a clastic section; therefore, a velocity increase westward toward the source of the fan is a reasonable expectation. Although the average velocity may

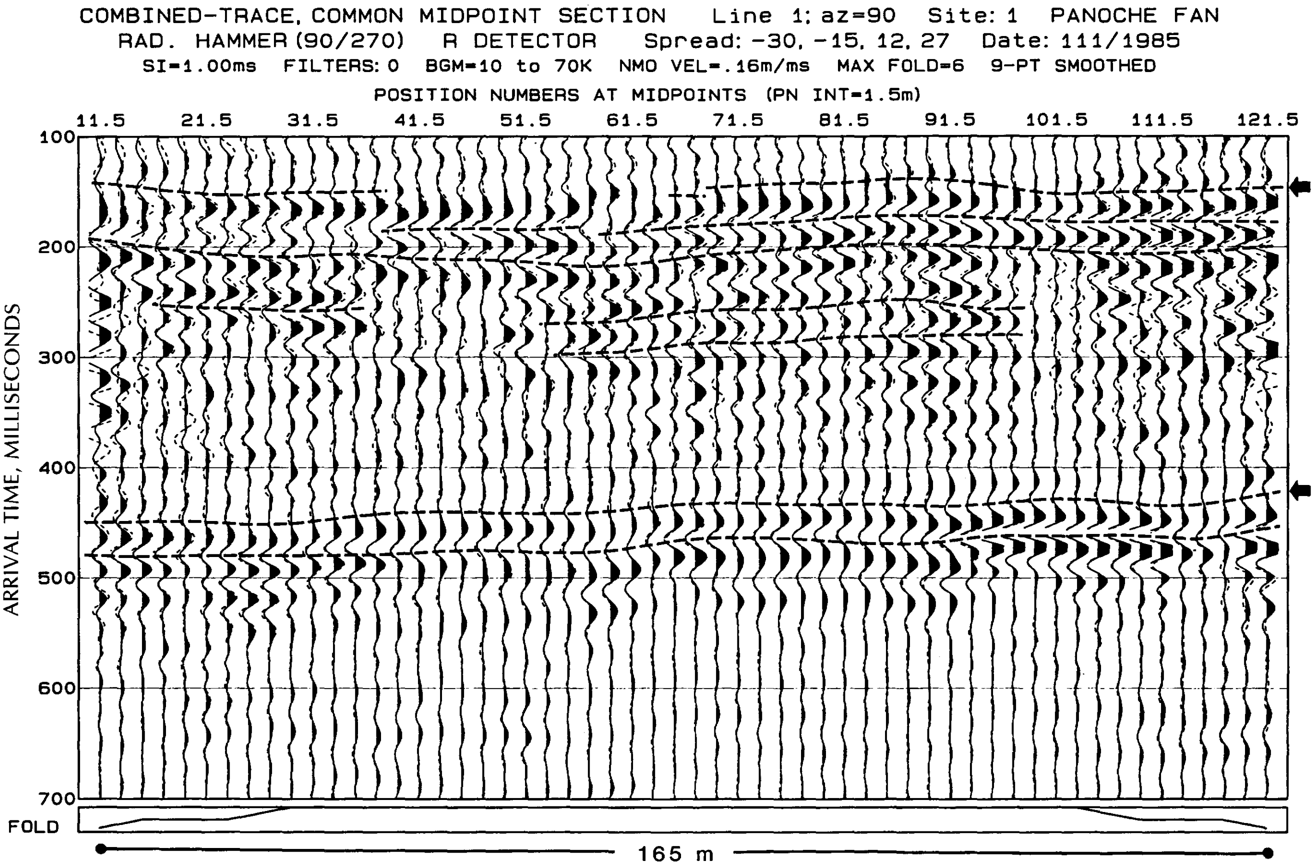

Figure 29.3. Radial-source/radial-seismometer, shear-wave, combined-trace, common-midpoint (CMP) section at seismic site 1, Panoche fan area, California. Horizontal distance between the traces is 3 m, total section distance is 165 m, and depth using a constant velocity of 0.16 km/s ranges from 8 to 56 m (a vertical exaggeration of approximately 2:1). Amount of fold applied in the CMP process is indicated on the fold diagram across the bottom of the section.

change from one end of the section to the other, it is highly unlikely that significant velocity differences occur within the 3-m spacing between traces on the section. Thus, the lenslike appearance of the seismic traces of the lower horizon at positions 91.5 to 111.5 (a distance of 30 m) is probably real. If it is, note that, with this shear-wave seismic method, we are detailing a structure that has a relief of only about 1 m.

It is tempting, but very unwise without drill data, to infer that the interpreted seismic horizon at a depth of about 15 m (upper arrow on fig. 29.3) and the top of the low-resistivity layer at about the same depth are geophysical expressions of the clay layer. If this horizon is the top of a clay layer, then the seismic section indicates that the clay is discontinuous across the section, in contrast to the reflection horizon beneath it at about 200 ms.

The block of reflection arrivals at about 260 ms and ranging from position 52 to 100 appears to be separated from its neighbors. If minor faulting occurred in this immediate area, then the zones of amplitude loss bounding this block of reflections can be interpreted as fault indicators. A fault of small throw can be interpreted downward and to the left from position 63.5 at 120 ms to the zone of low amplitude at 250 ms and a position between 45.7 and 47.5. A more likely interpretation is that lateral changes in seismic character result from stratigraphic variations.

COMMENTS

The Panoche fan is almost featureless and is heavily farmed. Thus, traditional stratigraphic studies of it are restricted to what can be seen at its edges and to what can be observed from borehole logs. It would be prohibitively expensive to seismically survey the entire fan; however, for those problem areas within which detailed stratigraphic correlation between boreholes is critical, seismic results of the quality shown on figure 29.3 would be helpful.

The question as to what changes in physical properties occur within this section will remain unresolved until borehole data have been obtained. Of particular interest in the seismic studies is the probable acoustic difference leading to a shear-wave reflection from the clay layer. I suspect that the clay layer will prove to be of lower velocity, following the generality that finer grained clastics have lower velocities than coarser grained clastics. If this is true, then refraction methods, because they require a high-speed layer as a target, are not recommended for mapping the clay layer. Reflection methods require existence of differences in acoustic impedance (the product of velocity and density) across boundaries, a condition that may be met by a clay layer sandwiched between layers of coarse-grained sediments.

P and S waves, in addition to their differences in particle motion, differ in their seismic behavior within the Earth. Within a section of unconsolidated rocks, the top of the saturation zone probably will be detected by P-wave methods, but this hydrologic boundary will be transparent to S-wave techniques. In broad terms, S waves respond to differences in lithology, whereas P waves respond to differences in both lithology and fluid content. For study of the near-surface section, it seems that the best course is to more fully investigate use of both methods in combination, an extra benefit being derived through use of v_P/v_S ratios to obtain a measure of rock strength.

As Bisdorf (this volume) has pointed out, electrical resistivity in this area appears to be a function of grain size, lower values of resistivity being associated with the finer grained materials. If a triple functional relationship can be established between stratigraphy, resistivity, and velocity in this area, then two possibilities emerge:

1. Combined use of electrical and seismic methods may be used to map interborehole stratigraphy—in particular, the distribution of the clay layer and the location of old stream channels that may act as pathways for contaminated waters.
2. The resistivity maps may be used to delimit lateral velocity variations and thus permit time sections to be converted to more realistic representations as depth sections.

CONCLUSIONS

Results obtained during the initial test program indicate that, with proper design of data acquisition and processing procedures, shallow, high-resolution reflection seismics can be developed into a useful tool for detailing stratigraphic variations between geologically and geophysically logged drill holes located within reasonable distances from each other.

30. Relation of Selenium at Kesterson National Wildlife Refuge to Potential Soil-Forming Source Rocks

By T.S. Presser

The west side of the San Joaquin Valley of California has been identified as an area where selenium has been dispersed from soil-forming formations in the California Coast Ranges. Because of climate, soil type, presence of alluvial clay layers, emplacement of subsurface drains, availability of imported irrigation water, type of irrigation, and the unique chemical properties of selenium, selenium has been biogeochemically cycled. This process has taken place throughout geologic time in both the Coast Ranges and their alluvial fans and, on a smaller time scale but in a more complex way, in the ponds of Kesterson National Wildlife Refuge (KNWR), a refuge situated in the valley trough. The effects of elevated levels of selenium are seen at KNWR in all parts of the ecosystem, including bioaccumulation in the food chain and a 64-percent rate of deformity and death in embryos and hatchlings of wild aquatic birds (Ohlendorf and others, 1986). Other larger areas of wetland habitat in the flood plains of the San Joaquin River are also affected, namely the Grassland, which encompasses 52,000 acres. Because the pathway of agricultural drainage includes the San Joaquin River, the San Francisco Bay, and the California Aqueduct, other ecosystems and even human health may be affected.

Studies of the chemical and isotopic relations and water and rock reaction data have been completed on water samples from the ponds at KNWR, on subsurface agricultural inflows to the San Luis Drain, which is the supply canal for the KNWR ponds, and on irrigation supply waters in the surrounding area (Presser and Barnes, 1984, 1985). For the nine actively inflowing waters to the San Luis Drain from the west, Kesterson pond 2, and the San Luis Drain, the correlation coefficient of linear regression between sodium and sulfate is 0.99 and between dissolved sulfate and selenium is 0.93. Percent sodium ranged from 55 to 92 percent of the total cations, and sulfate from 54 to 85 percent of the total anions present in the waters. The highest concentration of sulfate was 22,500 mg/L. Selenium concentrations ranged from 140 to 1,400 μg/L. Selenium was found in these waters to be predominantly (up to 98 percent) in the form of selenate ($SeO_4^{=}$) where selenium is in the +6 oxidation state, its highest oxidation state. Care must be taken in selection and execution of methodology for analysis because different sensitivities may be exhibited for Se^{+4} and Se^{+6} in spectral analysis, and organic selenium compounds may be easily volatilized. It was estimated that failure to include the reduction step in the hydride generation technique for analysis of selenium in water may account for as much as 98 percent of the total selenium being left undetected in agricultural drainage water (Presser and Barnes, 1984).

From reaction states in water for various minerals (Kharaka and Barnes, 1973), gypsum ($CaSO_4 \cdot 2H_2O$), mirabilite ($Na_2SO_4 \cdot 10H_2O$), and thenardite (Na_2SO_4) were found to be associated with waters on the valley floor. Gypsum used locally as a soil amendment contained more than 0.5 parts per million (ppm) selenium. Thenardite and an algal mat from Kesterson pond 1 contained 1.8 and 13 ppm selenium, respectively, reflecting both inorganic and organic (food chain accumulation) uptake of selenium. Thenardite was also identified as a salt crust at the location that exhibited the highest concentration of selenium in the inflow waters to the San Luis Drain; the salt contained 17 ppm selenium. These minerals have also been identified in the Coast Ranges bordering the western San Joaquin Valley in 1977 (Murata, 1977) and more recently in our own studies. In both studies, magnesium sulfates and mixed sodium and magnesium sulfates were also found. Because of the similar chemical and physical properties of sulfur and selenium, the inorganic uptake of selenium in these sulfate evaporite or efflorescent minerals is now being evaluated as part of continuing research on the geologic source of selenium. Ground-water and stream chemistry is complex in the Coast Ranges and reflects several different regimes besides marine sediments; these include ultrabasic intrusive rocks, epithermal zones of mercury ore deposition (New Idria), and the Franciscan Formation. Potential transport mechanisms of selenium include runoff and mass wasting of sediment and salts to the valley alluvium, mostly during flood events.

The more insoluble weathering products found in the Coast Ranges, limonite, jarosite, and alunite, and minerals including pyrite from the cuttings of a 16,000-foot core of a well from the alluvium of the west side of the valley in the area of concern are also being studied. The amount of selenium in these minerals will be quantified. The oxidation state of selenium in these minerals as a function of diagenesis and weathering must also be analyzed to evaluate mechanisms of inclusion. Solution-precipitation behaviors and concentrating mechanisms of these different minerals are then, in turn, important in quantitating the major paths by which selenium moves.

The approach to elucidating the source of selenium and the mobilization, concentration, and transport mechanisms in the Coast Range formations will also include isotopic analysis. Study of the isotopes of water shows possible sources and history of the water. Isotopic relations of D/H and $^{18}O/^{16}O$ in waters in the vicinity of KNWR yielded an evaporation trend line whose slope was comparable to those of desert basins. The clustered points for the inflow waters to the San Luis Drain, indicating similar histories for the waters, fell between the depleted waters of the irrigation supply canals and the enriched waters of the KNWR ponds with a correlation coefficient of 0.99.

Ultimately, isotopic studies of source formations can be diagnostic and confirmatory of selenium sources and sinks and the path by which selenium moves into the ground water. The isotopes of both strontium ($^{87}Sr/^{86}Sr$) and selenium ($^{82}Se/^{76}Se$) are possible candidates for this tracer work. Methodology and data for strontium ratios in rocks are available (Faure and Powell, 1972); fewer data exist for ratios in waters (Stettler and Allegre, 1978). Relations of selenium concentrations and strontium fractionations may be seen in source rocks, waters, and alluvial material. Methodology for measuring selenium ratios is less well tested (Hoefs, 1980, p. 51–52) and is more complex, because of the large number of possible oxidation states for selenium. Transport of selenium entirely in the saturated zone (ground water) versus the unsaturated zone may be differentiated by opportunities afforded for fractionation.

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31. Heavy-Metal Accumulations in Sediments of Boston Harbor, Massachusetts

By Michael H. Bothner

Boston Harbor, Mass., is a prime example of an urban estuary in which environmental conditions have seriously deteriorated as a result of industrial and domestic waste discharge. In recent years, large areas of the harbor have had to be closed to shellfishing. In addition, a large number of winter flounder from the harbor have been found to have some type of liver cancer (Murchelano and Wolke, 1985). Recent legislation will eliminate Boston's two antiquated primary sewage treatment plants and the scattered storm drains that carry untreated wastes during periods of high runoff. A secondary sewage treatment plant, targeted for completion by the year 2002, is designed for ocean discharge of treated liquids and a land-based disposal of solid wastes.

Heavy metals represent one class of contaminants present in high concentration in the effluent discharged into Boston Harbor. The wastes discharged by the two operating sewage-treatment plants are the largest source of metals and sediments emptied into the harbor. These discharges have resulted in a significant increase in metal concentration in sediments, compared with average crustal abundances and with clays deposited before the industrial revolution (fig. 31.1). Profiles of metal concentration in sediment cores show a dramatic increase from background levels in buried sediments of preindustrial age to concentrations as much as 20 times higher than background in surface sediments (fig. 31.2). The elevated concentrations of heavy metals in sediments have been used to identify areas of the harbor where wastes accumulate.

We have made some preliminary attempts to interpret the history of metal deposition on the basis of ^{210}Pb dating, supplemented, in a few cores, by ^{137}Cs analysis. At most locations in the harbor, the radioisotope profiles in sediment cores suggest that the sediments are being mixed by biological and (or) physical processes that complicate the determination of accumulation rates. At one location in Hingham Bay, however, profiles of both isotopes suggest that sediments have been accumulating at a rate of about 2 cm/yr for approximately the last 70 years (fig. 31.3).

The limited data indicate that the recent rates of sediment accumulation are much faster than the rates one would predict from the thickness of unconsolidated sediments deposited since sea level rose following the last glacial period. Faster rates during the last century may reflect the increasing load of solid wastes discharged to the harbor, the increased biological scavenging of suspended particulate matter stimulated by additional nutrients, and the extensive engineering projects in and around the harbor (Fitzgerald, 1980).

Participants at a symposium that reviewed the marine research conducted in Boston Harbor (Kaufman, 1985) identified a critical need for a much better understanding of the oceanographic processes in Boston Harbor and Bay. A comprehensive monitoring program that includes all the subdisciplines of oceanography, tailored to the specific needs and problems of Boston Harbor, is being discussed by the symposium coordinators.

This program should address the following geochemical questions, which pertain to toxic organic compounds, as well as to metals: (1) Where and at what rate are waste discharges accumulating? (2) How are contaminants partitioned among surficial sediments, mobile suspended particulates, and dissolved phases? (3) What are the transport pathways and fate of contaminants added to the system? (4) What is the concentration of contaminants in interstitial waters, and can contaminated sediments continue to be a source of metals and toxic organic compounds after the primary sources are reduced or eliminated? (5) What is the rate of sediment accumulation in areas that are strongly influenced by bioturbation? (6) Which meteorological or oceanographic events are responsible for redistributing contaminated sediments, and can redistribution by any process have an adverse impact on the living resources of the harbor?

There is the capability in the U.S. Geological Survey for studies that can be an important supplement to both environmental geochemistry and to any comprehensive monitoring program initiated in Boston Harbor or in any other estuary. These studies include (1) synoptic time-series measurements to determine the flow regime and sediment transport (Butman and others, 1979); (2) seismic-reflection and sidescan-sonar profiling to define the shallow sedimen-

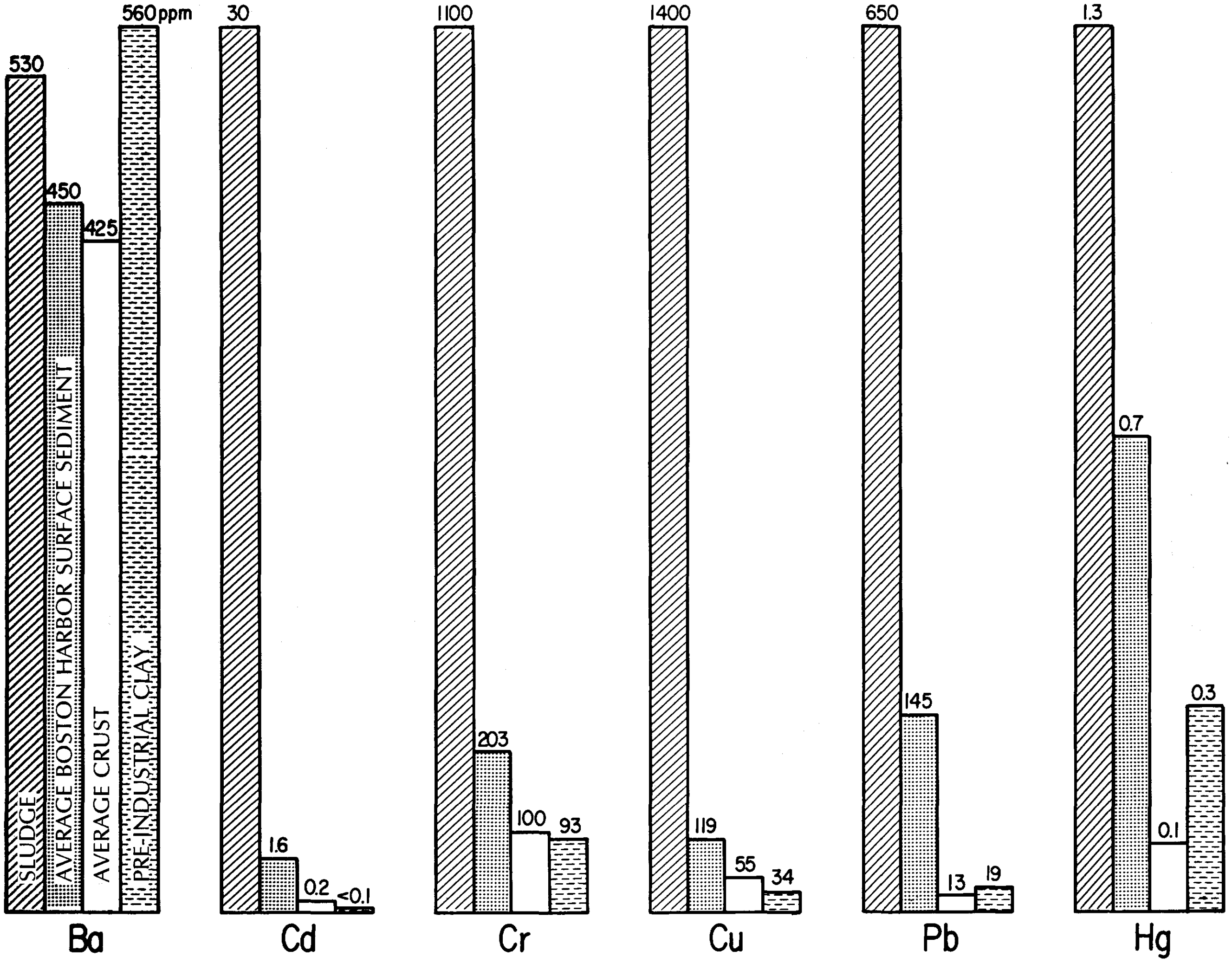

Figure 31.1. Relative concentrations (in parts per million (ppm)) of metal in digested sewage sludge from the treatment plant in Boston, Mass. (diagonal pattern), average concentration in the upper 2 cm of sediment (dots), concentration in average crustal rocks (no pattern) (Krauskopf, 1967), and concentration in clay (dashes) collected approximately 2 m below sediment surface in Boston Harbor. Barium is a metal not used by industry in the Boston area.

tary framework and long-term sedimentary processes that have operated in estuaries (Knebel and others, 1981; Knebel and Scanlon, 1985); and (3) geotechnical studies of estuarine sediments that can contribute critical information on the erodability of sediments and for the siting of pipelines and offshore structures (Booth and others, 1984).

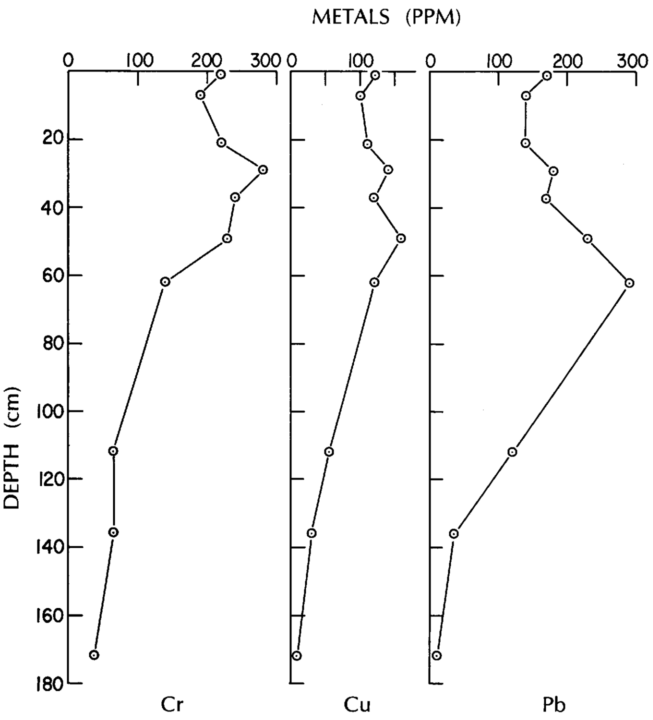

Figure 31.2. Profiles of metal concentration plotted against sediment depth in a core collected from Hingham Bay in Boston Harbor, Mass.

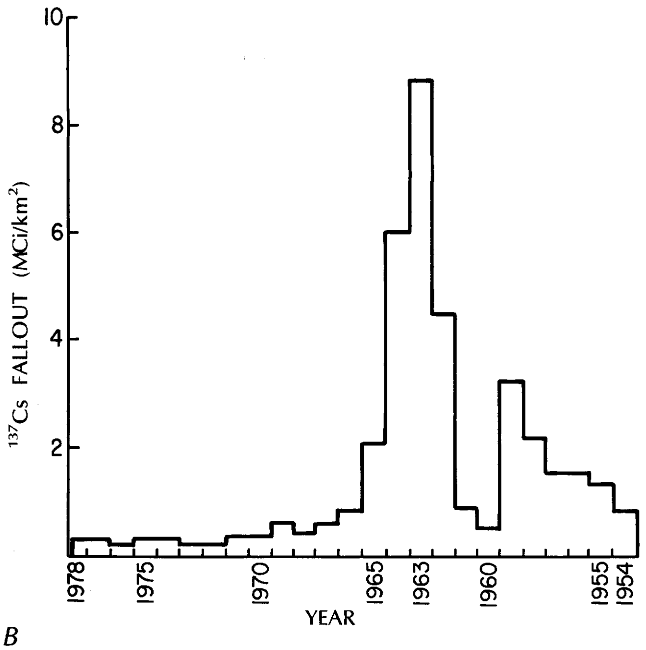

Figure 31.3. *B*, Fallout record for ^{137}Cs measured in New York City between 1954 and 1978. The preservation of the fallout peak in the sediments suggests that biological mixing of the sediments is not severe at this location and that the sedimentation rate is about 2 cm/yr in agreement with estimates derived from the profiles of ^{210}Pb.

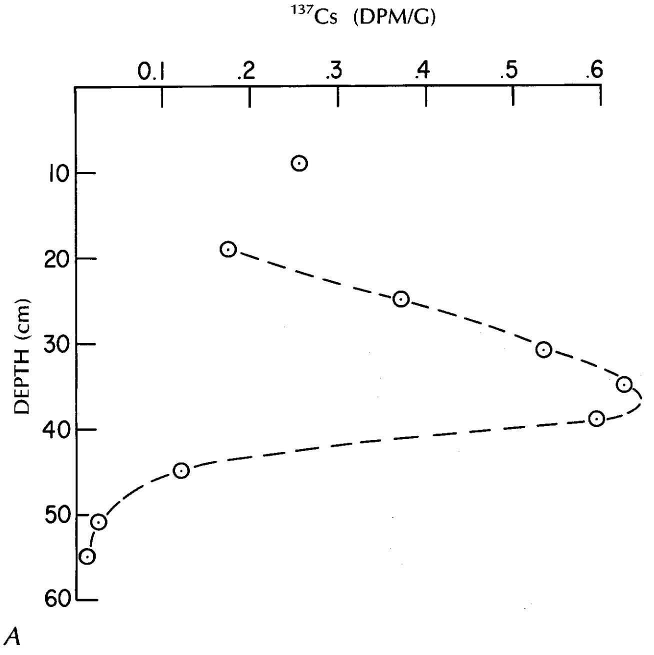

Figure 31.3. *A*, Profile of ^{137}Cs activity plotted against sediment depth in a core collected from Hingham Bay in Boston Harbor, Mass.

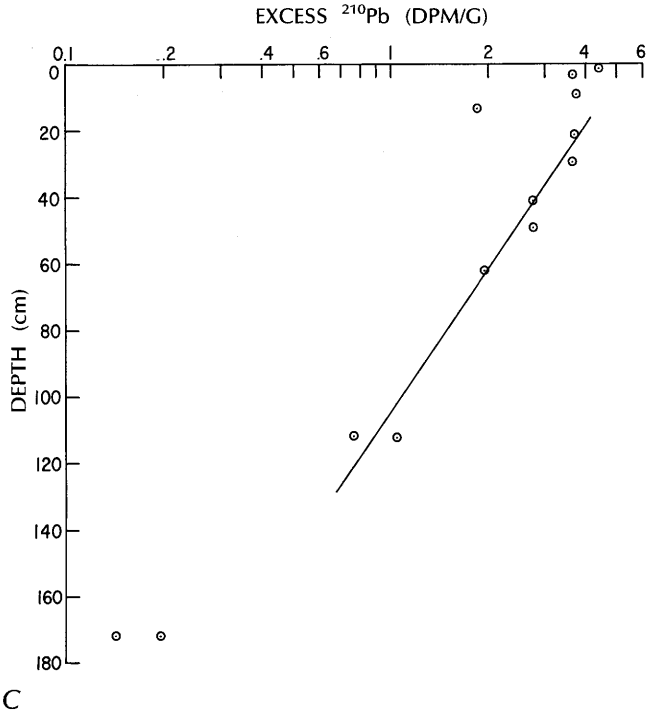

Figure 31.3. *C*, Profile of excess ^{210}Pb with sediment depth (same location as core in figure 31.3*A*). If sediment mixing is assumed to be minor and restricted to the upper 10 cm of sediment, the average is about 2 cm/yr. DPM/G, disintegration per minute per gram.

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32. New Bedford Harbor and Buzzards Bay—Transport of Pollutants on Fine-Grained Marine Sediments

By Bradford Butman

The transport of fine-grained sediment particles in the coastal ocean is a major factor in determining the long-term fate of pollutants introduced into the marine environment (such as polychlorinated biphenyls (PCB's), heavy metals, and polyaromatic hydrocarbons, and so on), which are strongly adsorbed by these particles. Transport of particles is determined by the physical characteristics of the material (size, density, shape, and settling velocity), by the spatial and temporal distribution of currents strong enough to resuspend the particles or weak enough to allow them to settle, by the circulation patterns that carry the suspended particles, and by biological processes that can mix the sediments on the sea bed and can alter the physical characteristics of the sediment by reworking or binding the particles. The distribution of sediments in the marine environment is the long-term result of these physical and biological processes.

Buzzards Bay, a semienclosed coastal bay about 40 km long and 15 km wide, is located along the southern Massachusetts coast (fig. 32.1). The bay is open to Rhode Island Sound to the southwest and to Vineyard Sound to the south and southeast through several small passages between the Elizabeth Islands. The water is 20 m deep near the mouth of the bay and gradually shoals to less than 5 m deep at the head. The bottom sediment distribution in the bay is complex and reflects the glacial history of the area, as well as modern physical processes (Moore, 1963; Robb and Oldale, 1977). Fine-grained silt and clay are found along the axis in the deeper part of the bay, and mixtures of sand, silt, and gravel are distributed around the perimeter of the bay and near the mouth where the topography is more rugged.

New Bedford Harbor is located along the western shore of Buzzards Bay in the Acushnet River estuary (fig. 32.1). Between about 1950 and 1970, two manufacturing firms discharged large quantities of PCB's to New Bedford Harbor. As a result, sediments in the inner harbor are heavily contaminated with PCB's (Farrington and others, 1985); concentrations in the surficial sediments are as high as 1,250 parts per million (ppm), and concentrations in commercial fish species are as high as 26 ppm (the Food and Drug Administration's limit for human consumption is 5 ppm). Mussels analyzed as part of the Environmental Protection Agency's (EPA) Mussel Watch program contained PCB's in concentrations as high as 49 ppm, at least 50 times higher than concentrations found at other urban East Coast locations and 1,000 times higher than those found at pristine locations (Farrington and others, 1985). Although there is only a limited exchange of water and particles through the hurricane barrier at the mouth of the harbor (see fig. 32.1), PCB's are found in the sediments and water column and in organisms in Buzzards Bay near New Bedford. Typical concentrations are 0.1–1.0 ppm in the sediments and 1–10 parts per trillion in unfiltered water. Inner New Bedford Harbor is closed to all fishing, and portions of the outer harbor and Buzzards Bay are also closed to certain fisheries (fig. 32.1). New Bedford Harbor was declared an EPA Superfund site in 1982.

The long-term fate of PCB's is partially determined by the physical and biological processes that transport water and fine-grained sediments from the inner harbor to Buzzards Bay and throughout the bay. The currents in the bay can be conceptually separated into a seasonal flow, low-frequency currents driven by wind and the density field, tidal currents, and high-frequency currents associated with surface and internal waves. Preliminary analysis of pilot field measurements made by investigators at the U.S. Geological Survey (USGS) and the Woods Hole Oceanographic Institution by using specialized near-bottom instruments (fig. 32.2) (Butman and Folger, 1979; Williams, 1985), current meters, and other techniques provides some information on these currents, illustrates their temporal and spatial variability, and identifies some of the important processes causing sediment transport in the bay (Signell, 1987; Rosenfeld and others, 1984). The observations suggest a complex residual flow pattern composed of small circulation cells that may be partially driven by the tidal circulation. Net near-bottom current speeds associated with

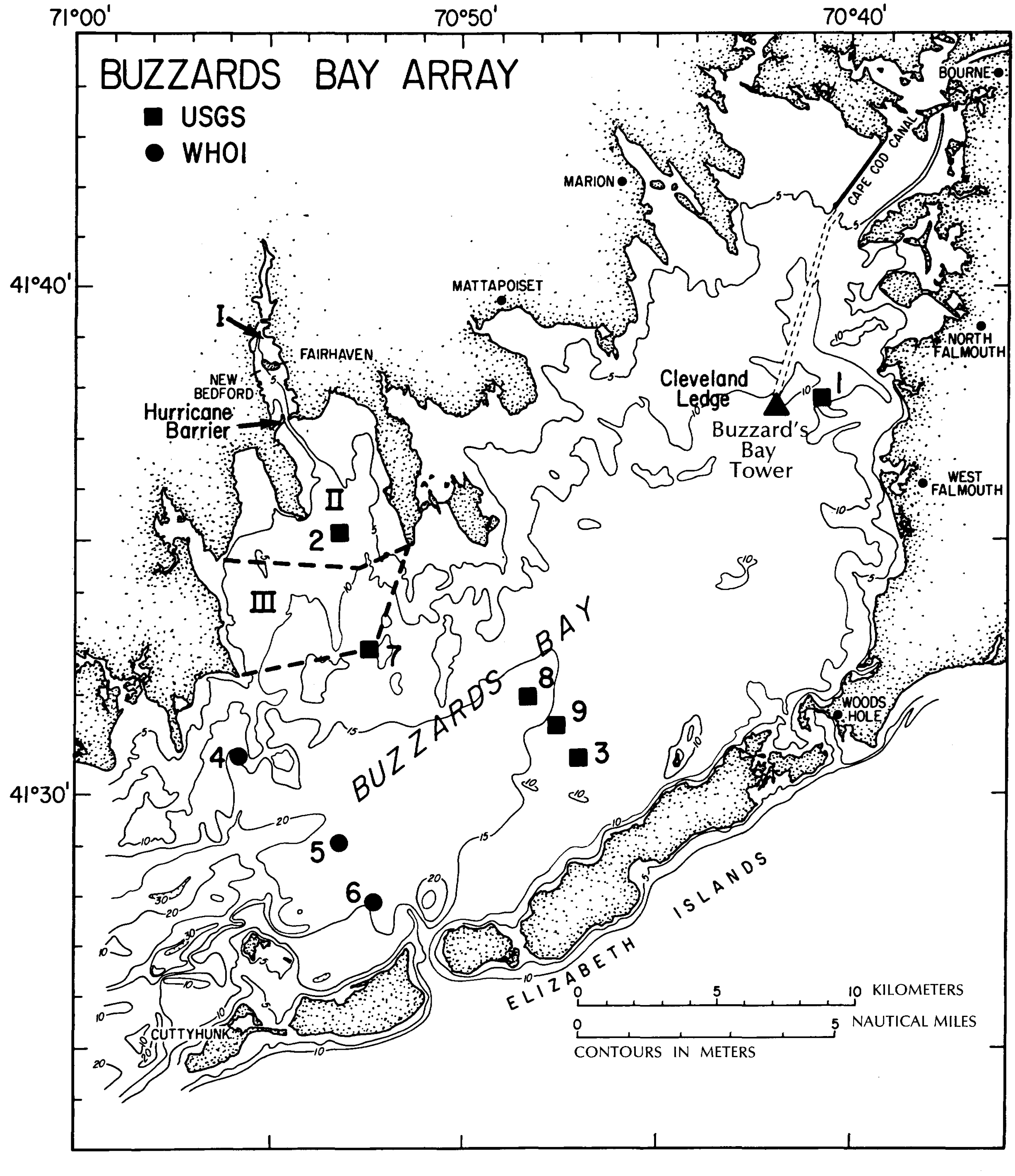

Figure 32.1. Buzzards Bay, Mass., showing locations where current or near-bottom sediment movement observations have been made. The measurements by the U.S. Geological Survey (USGS) were made at stations 1, 3, 7, 8, and 9 during 1984–85. Regions closed to fishing activity because of polychlorinated biphenyl (PCB) contamination are Area I (closed to all fishing, shellfishing, and lobstering), Area II (closed to bottom-feeding finfishing and lobstering), and Area III (closed to lobstering). The highest levels of PCB's are found near New Bedford to the north of the Hurricane Barrier. Adapted from Robb and Oldale (1977) and from National Ocean Survey chart 13230. WHOI, Woods Hole Oceanographic Institution.

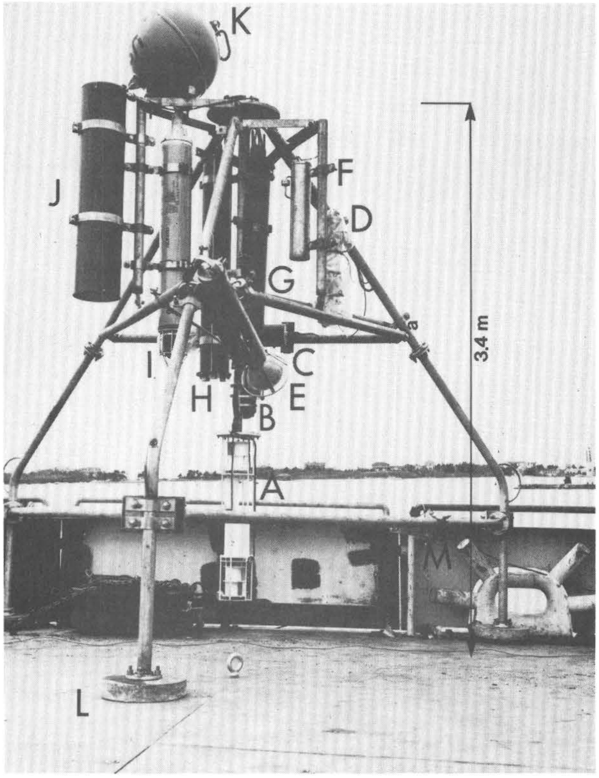

Figure 32.2. Bottom tripod system designed for studies of near-bottom sediment transport. The system measures current, temperature, light transmission, and pressure and photographs the sea floor. The instruments have been used extensively on the continental shelf to document processes of sediment transport. A, current sensor; B, pressure sensor; C, transmissometer; D, camera; E, camera strobe; F, camera battery; G, data logger; H, battery pack; I, acoustic release; J, rope canister; and K, recovery float.

this residual circulation are on the order of 1–5 cm/s, and water-particle displacements are on the order of 1–5 km/d; thus, particles transported with the residual flow can travel across the bay in a few days. The tidal currents are dominated by the M_2 (semidiurnal, period of 12.42 hours) tide; their speed is about 25 cm/s near the mouth of the bay and decreases to less than 10 cm/s near the head. Neither the residual circulation nor the tidal currents are strong enough to resuspend the existing sediments by themselves, except perhaps during spring tides near the bay mouth. However, intense near-bottom sediment resuspension and transport do take place during strong storms (fig. 32.3). During these storms, oscillatory currents associated with surface waves are primarily responsible for increasing the bottom stress above the critical value for sediment resuspension (see Grant and Madsen, 1979, and Butman, 1987, for a description of the effect of surface waves on bottom stress). Once resuspended, the sediments are transported in the direction of the wind-driven currents. At least for the central part of the bay, the near-bottom currents during intense storms flow opposite to the wind. A working hypothesis is that the storm-driven flows will distribute fine-grained sediments to the central part of the bay; escape from Buzzards Bay to Rhode Island Sound may occur only during strong winds from the southwest when waves are large because of the long fetch and net near-bottom flow is opposite to the wind (out of the bay). These observations on sediment transport are typical of other coastal areas where sediment movement is episodic and the net transport is the cumulative result of many transport events.

The transport of PCB's in Buzzards Bay is just one example where a detailed understanding of the dynamics of particulate transport in the coastal ocean is important in assessing the long-term effects from localized pollutant sources and in devising remedial strategies for cleanup. Discharge of sewage effluent and sludge (for example, into Boston Harbor; see Bothner, this volume) and dumping of dredge spoil or drilling muds into coastal waters are other examples. Important problems occur nearshore in coastal bays and estuaries, as well as offshore on the continental shelf and slope. Scientists in the USGS have already conducted extensive field studies of sediment transport along the U.S. East- and West-Coast continental margins (Drake and Cacchione, 1985; Butman, 1987; Bothner, this volume).

Studies to investigate the transport of fine-grained material provide an excellent opportunity to conduct sound research that has direct practical benefit. Comprehensive studies of particulate transport in the coastal zone should be multidisciplinary and include (1) geologic site characterization (bathymetry, high-resolution and side-scan sonar surveys, surficial sediment texture); (2) geochemistry (pollutant characterization, distribution between dissolved and particulate phases, sediment accumulation rates, mixing rates); (3) circulation and sediment transport (advection, resuspension, deposition); (4) biological processes in the water column and on the sea floor that affect particulate transport (mixing, repackaging, binding) and chemical composition. The mix of these various study components appropriate to a given area will depend on the particular transport problem. Scientists within the USGS are uniquely qualified to address these program components.

ACKNOWLEDGMENTS

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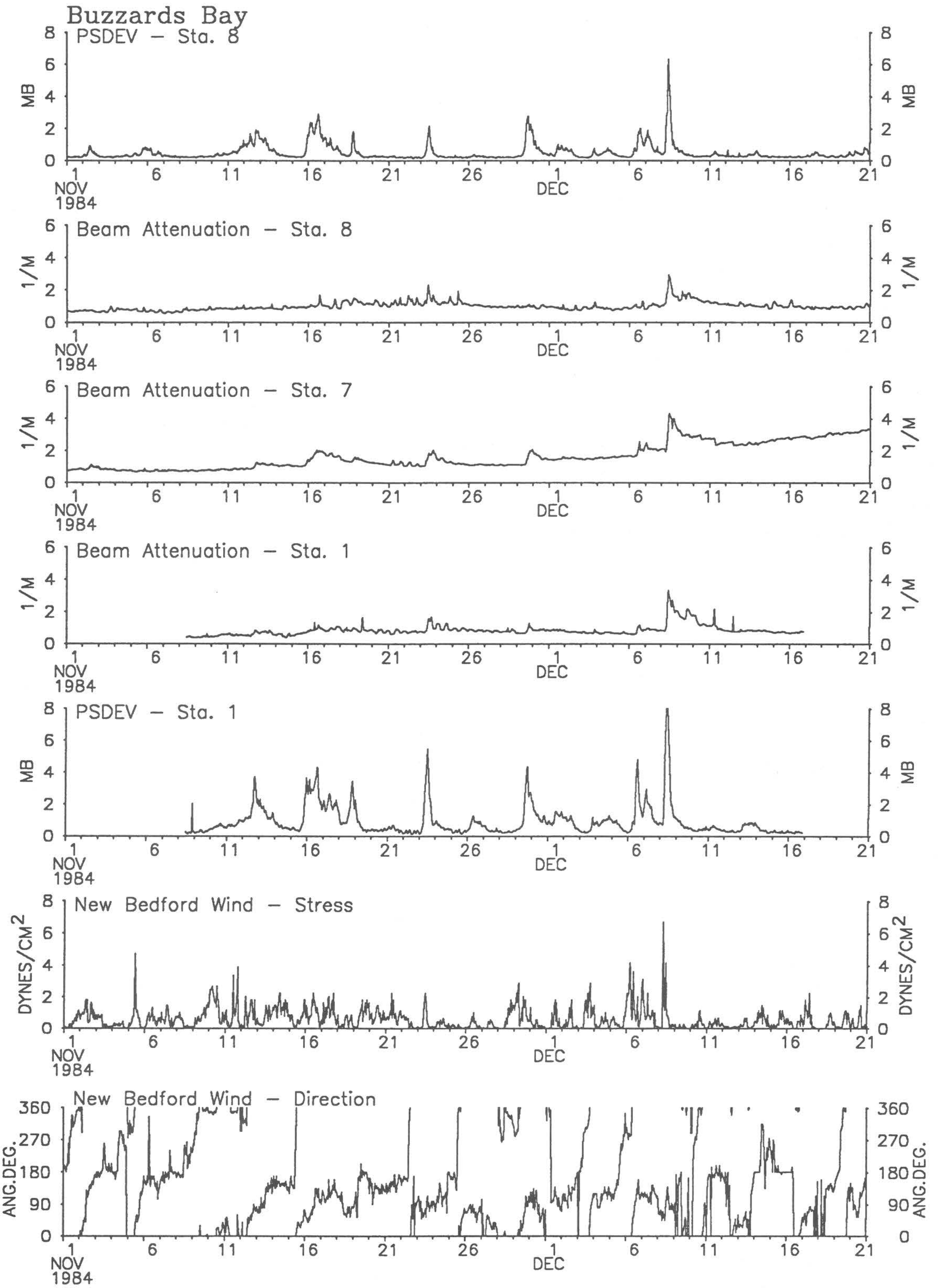
Buzzards Bay
PSDEV – Sta. 8
MB
Beam Attenuation – Sta. 8
1/M
Beam Attenuation – Sta. 7
1/M
Beam Attenuation – Sta. 1
1/M
PSDEV – Sta. 1
MB
New Bedford Wind – Stress
DYNES/CM2
New Bedford Wind – Direction
ANG.DEG.
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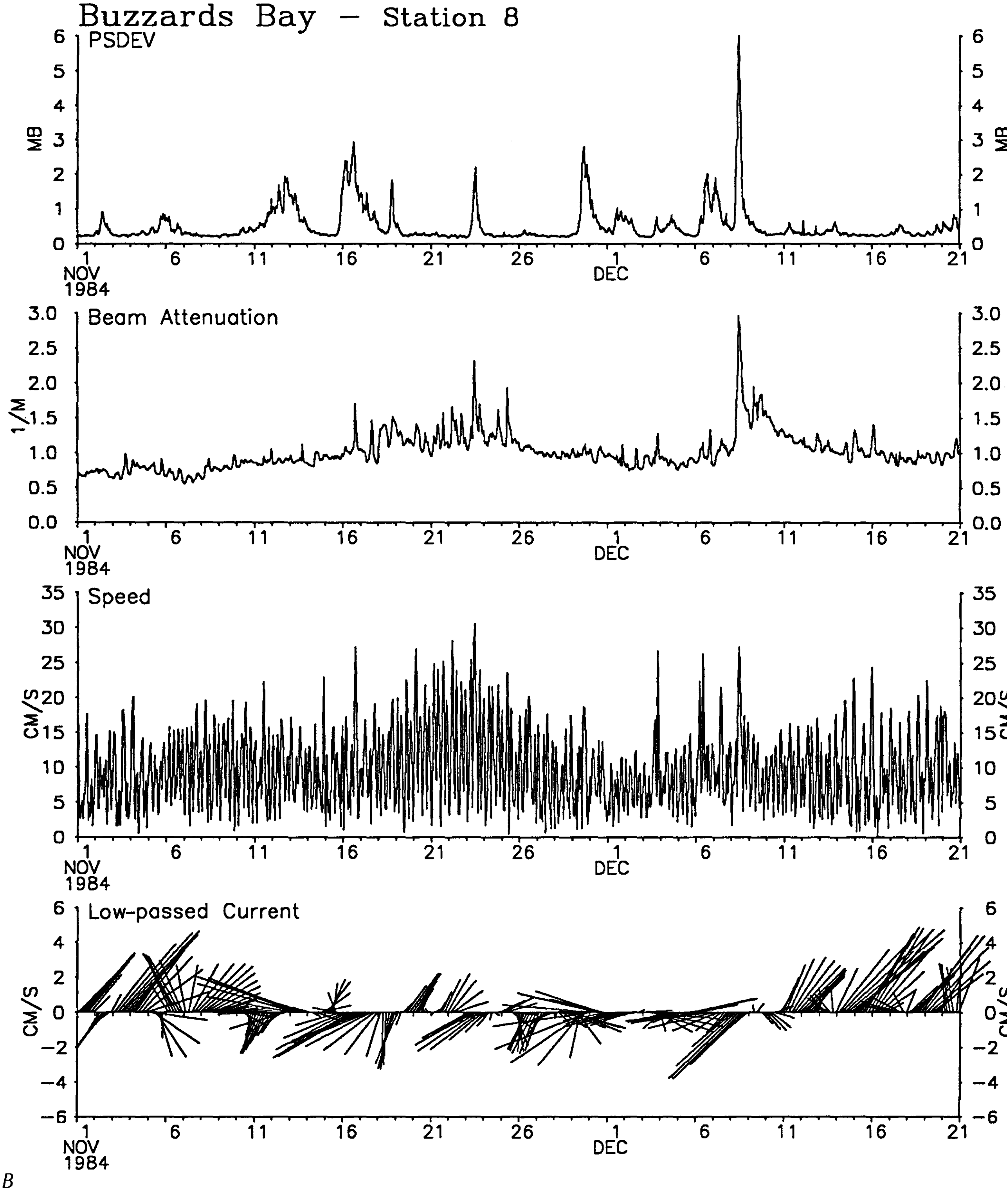

Figure 32.3. *A*, Beam attenuation (proportional to suspended sediment concentration) at stations 1, 7, and 8; near-bottom pressure fluctuations (PSDEV) at stations 1 and 8 (a rough measure of the amplitude of the waves near the bottom); and wind stress and direction at New Bedford, Mass., from November 1 to December 20, 1984. The observations clearly show the episodic resuspension of near-bottom sediments associated with waves, especially on December 8. *B*, Near-bottom wave fluctuations, beam attenuation 2 m above bottom, current speed 1 m above bottom, and low-passed current at station 8. The low-passed "stick" diagram shows the direction of the daily averaged flow (oscillatory tidal currents are removed). The current sticks originate along the time axis and point in the direction of net flow. MB, millibars; 1/M, inverse of meters; ANG. DEG., angles of degrees; CM2, cm^2.

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33. The Georges Bank Monitoring Program—Trace Metals in Bottom Sediments

By Michael H. Bothner

Exploratory drilling for petroleum resources in the rich fishing grounds off New England has always been controversial. When the plans for lease sale 42 (Georges Bank) were made known during the mid 1970's, a legal battle was initiated by fishing and environmental groups against the U.S. Department of Interior. Part of the settlement of this controversy was the creation of a Biological Task Force for Georges Bank, which had the responsibility of designing a monitoring program that would evaluate the environmental effects of offshore drilling and provide an early warning of adverse effects.

Part of the monitoring program was designed to establish the concentration of trace metals in sediments prior to drilling on Georges Bank and to monitor the changes in concentrations that could be attributed to exploration activities. Some of the specific questions addressed in this study were (1) Where do discharged drilling muds accumulate on Georges Bank? (2) How great an increase in trace metals results from accumulation of drilling mud? and (3) In areas where drilling-mud components accumulate, how long do they remain at an elevated concentration after the drilling is completed? Details of this study and the results of the other studies conducted as part of this comprehensive monitoring program are published elsewhere (Michael and others, 1983; Maciolek-Blake and others, 1985; Bothner and others, 1986; Phillips and others, 1987).

The first cruise of the monitoring program took place just before exploratory drilling commenced in July 1981, and subsequent cruises were conducted on a seasonal basis over a 3-year period. Samples were collected at regional stations 1–18 (fig. 33.1) and at 29 site-specific stations (fig. 33.2) centered around a drilling site.

The mean current flow on the southern flank of Georges Bank is to the southwest, parallel to depth contours, although the mean current can reverse in direction in response to storm winds or other oceanographic events (Butman and others, 1982). With respect to the mean current flow, transect 1 to the east is upstream, and transect 3 is downstream of the blocks offered in lease sale 42.

The chemistry samples were collected by means of a teflon-coated grab sampler. The upper 0–2 cm of sediment was analyzed for 12 trace metals. The only metal that showed a change in concentration as a result of drilling was barium. Barium is added to drilling mud in the form of the mineral barite ($BaSO_4$).

The barium concentrations in sediments at most stations within the site-specific survey (fig. 33.3) increased after the drilling began, just before cruise 3, and reached a maximum at the time of cruise 5, just after drilling was completed. Concentrations then decreased in the period following drilling. The maximum increase in the concentration of barium in bulk sediments (undifferentiated with respect to size) was from about 30 parts per million (ppm) to 132 ppm adjacent to this drilling rig and to 172 ppm next to the drill rig at station 16.

The detailed sampling and analysis have provided an opportunity to address a number of questions about the fate of drilling mud specifically and the fate of other pollutants in general that may be discharged on Georges Bank: (1) Where does it go? (2) How is it transported? and (3) How long does it persist near the site of deposition?

Increases in the concentration of barium in the bulk sediment were found 6 km away from the drill rig near station 5 (fig. 33.3) but were not observed at regional stations more distant from drilling locations. However, by analyzing the fine fraction (silt and clay) of the sediment for barium, we greatly increased our ability to detect small increases in barium. Within the fine fraction, we observed increases in barium concentration at stations 10 and 12 approximately 65 km west of drilling. We also measured an increase at stations 2 and 3, 35 km east of the easternmost drilling location, possibly in response to a reversal in mean current flow.

How is barium transported? We deployed sediment traps near the drill site after drilling was completed and caught material rich in barium. The spatial arrangement of the traps and the barium concentrations suggested that some of the drilling mud initially deposited near station 5–1 (fig. 33.3) was being resuspended by tidal and storm currents

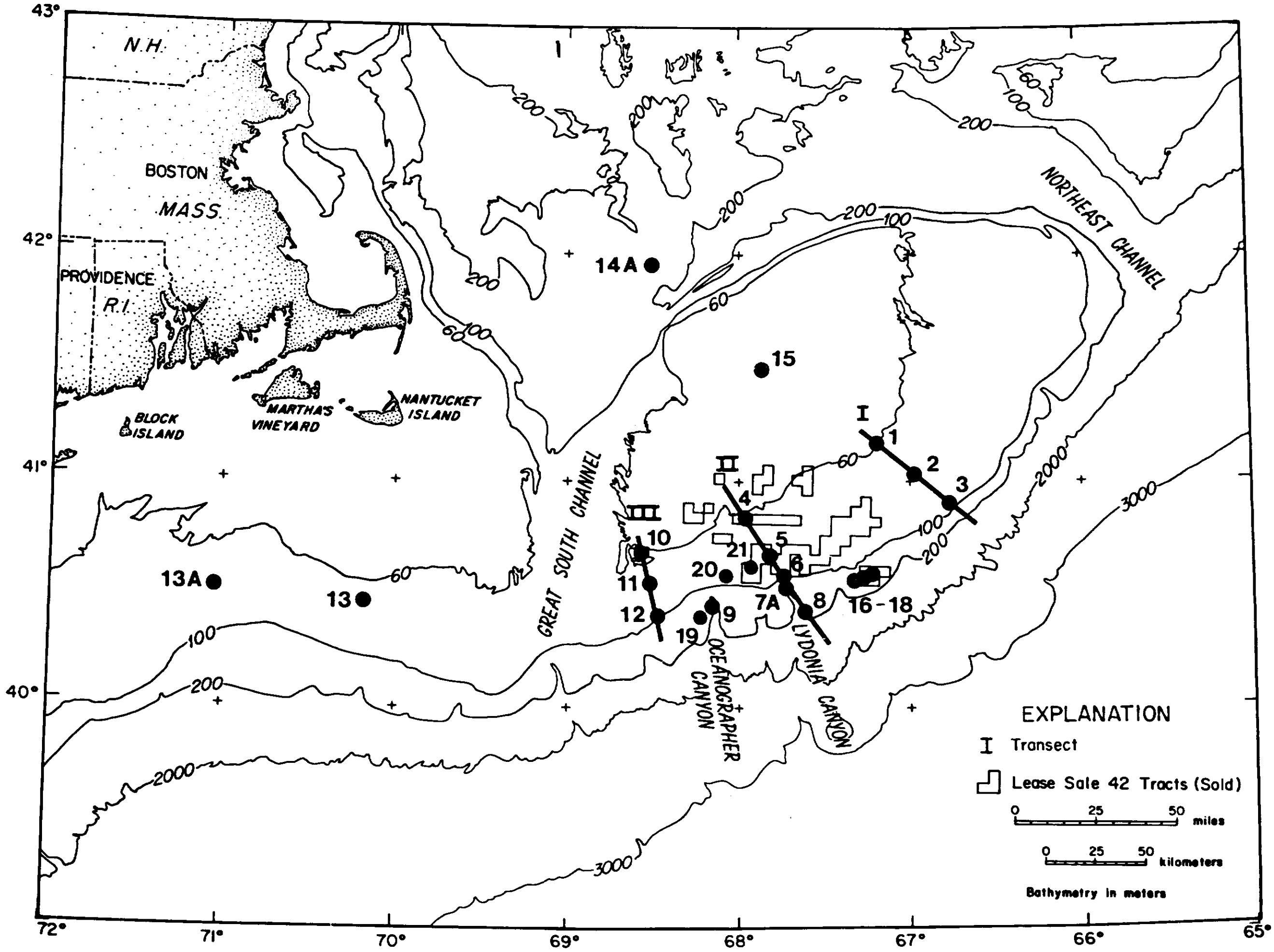
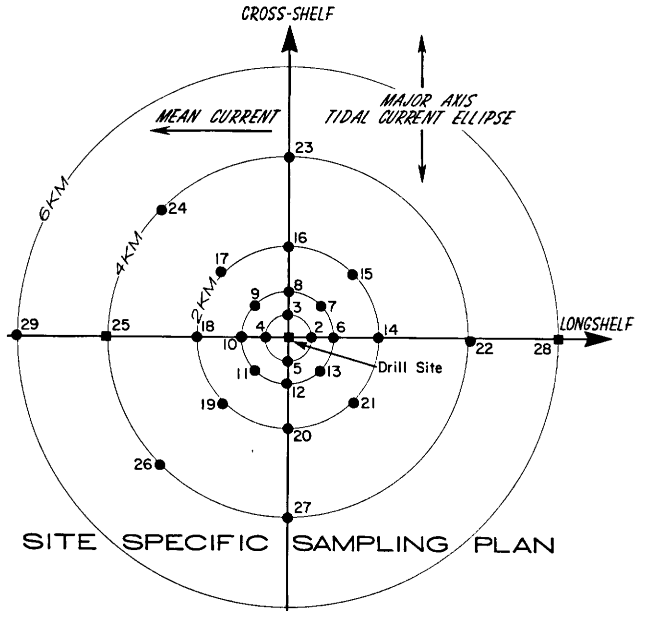


Figure 33.1. Regional sampling station array, Georges Bank. Site-specific array in block 312 is centered at station 5. Stations 15–21 sampled only once during this program. From Bothner and others (1986).



◀ Figure 33.2. Site-specific sampling station array around regional station 5 (block 312), Georges Bank. Stations 5–7, 5–13, 5–15, 5–17, 5–19, 5–21, 5–23, 5–24, 5–26, and 5–27 are secondary stations (of lower priority) and have not been analyzed routinely. From Bothner and others (1986).

and was carried in the water column. Transport of this material along the surface of the sea floor was probably taking place also.

How fast is the drilling-related barium removed from the surface sediments by natural processes? We computed an inventory of barite in the upper 2 cm of sediment by using the closely spaced stations within the 0.5- to 2-km annulus of the site-specific survey. The station closest to the drill site was excluded because of high spatial variability. By cruise 3, just after drilling began, the inventory of barite had increased from a background level of about 50,000 pounds and continued to increase until it reached a maximum of about 90,000 pounds just after drilling was

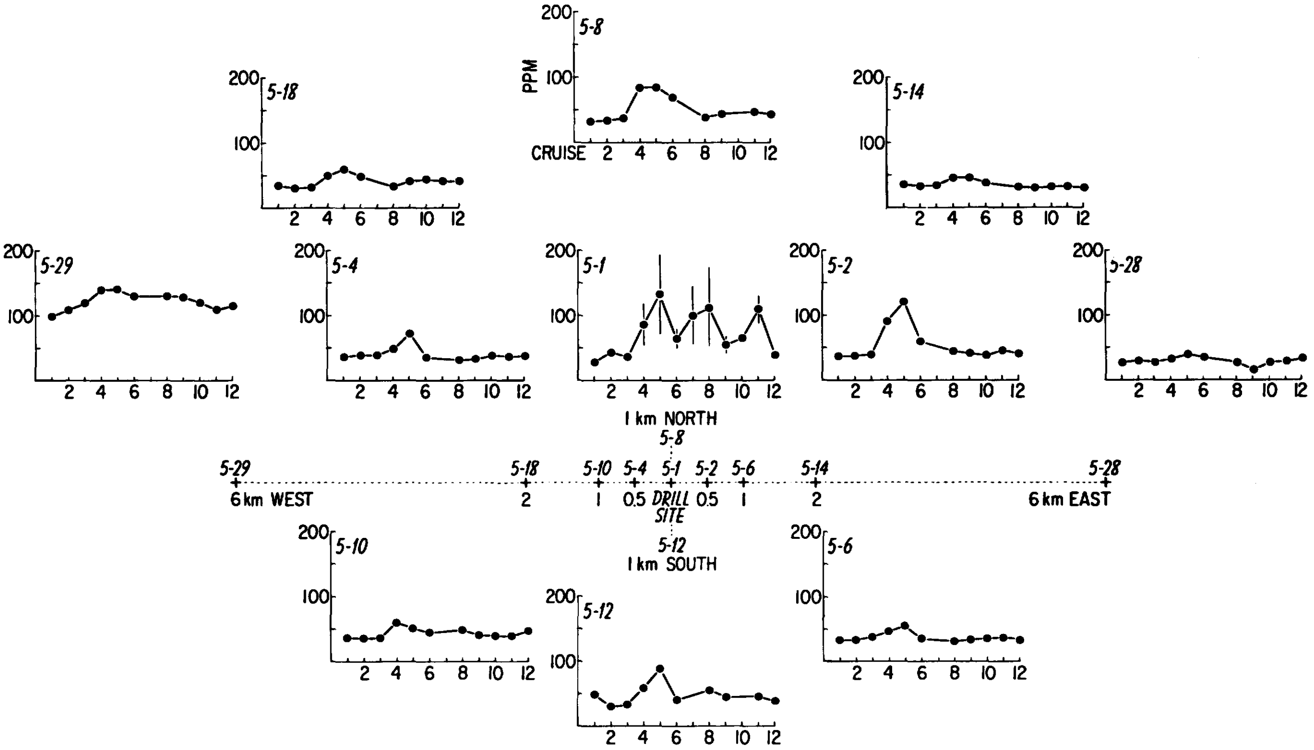


Figure 33.3. Concentrations in parts per million (ppm) of barium (circles) in bulk sediment on different sampling occasions near the drill site at block 312, Georges Bank. Stations are located on east-west and north-south transects through the drill site (see figure 33.2). Drilling began after the second cruise and ended just before the fifth cruise. Error bars are one standard deviation among three individual replicates. ND, no data. From Bothner and others (1986).

completed (cruise 5). The barium level then decreased to about 10 percent of the background by the end of the program (fig. 33.4). Replotting the net inventory (total minus background, fig. 33.5) on a semilog plot yields two straight lines from which half-lives can be calculated. For the first year following drilling, the removal half-life is 0.34 year; for the second year, it is 3.4 years. The slower rate for the second year may indicate that residual barite is coarser and (or) more deeply buried and transported only by more energetic storms, which are less frequent.

The rates of barium dispersal at station 5, located at 80-m water depth, are probably representative of the rates in other areas of the bank at comparable water depth. The rates may be faster in shallower water or slower in deeper water in response to the intensity of sediment transport processes (Butman, 1987).

In conclusion, this study has shown that, of the 12 trace metals analyzed in sediments, only barium increased as a result of drilling. The concentrations did not reach levels considered to be hazardous to benthic organisms. Because of the low toxicity of barium in the form of barite ($BaSO_4$), no adverse chemical stress to bottom-dwelling organisms is expected from the measured increases in barium concentrations. However, there is little information

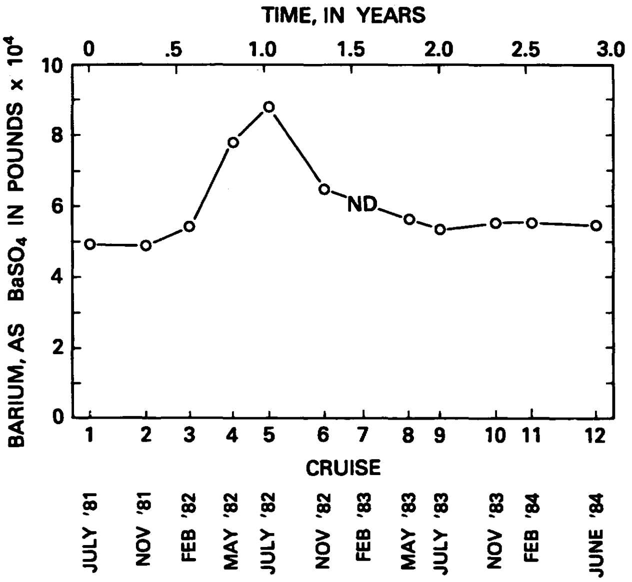


Figure 33.4. Total inventory of barite (calculated from barium concentrations) within the annulus between 0.5 and 2 km from station 5, Georges, Bank, on different sampling occasions. ND, no data. From Bothner and others (1986).

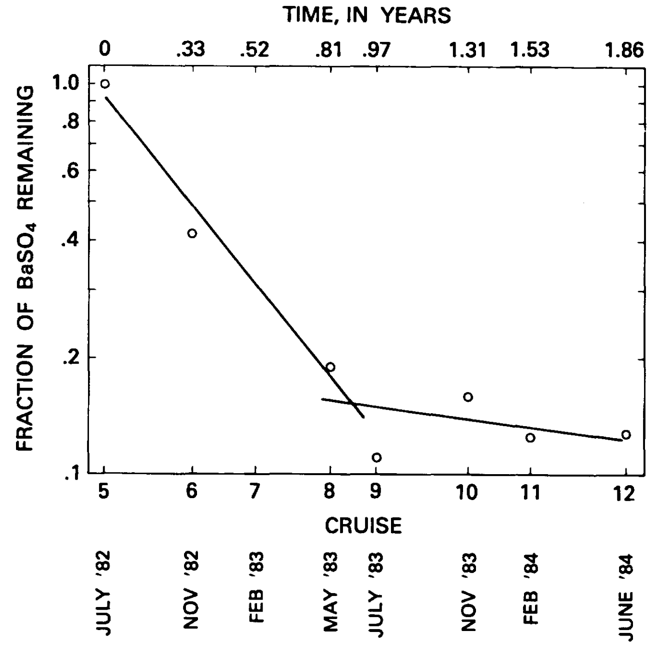


Figure 33.5. Decrease of the net barite inventory within the annulus between 0.5 and 2 km from station 5, Georges Bank, with time. Values are based on analyses of the bulk sediments. Fraction remaining is relative to the amount present at the time of cruise 5, 4 weeks after drilling was completed. From Bothner and others (1986).

concerning the effects on benthic organisms of long-term exposure to low concentrations of drilling mud. The biological studies of benthic organisms conducted as part of this monitoring program showed no effects attributable to drilling (Maciolek-Blake and others, 1985; Neff and others, in press). After drilling was completed, the energetic sediment transport processes on Georges Bank resuspended the barite from its location close to the drill rig and transported it to distances at least 65 km west and 35 km east of the drilling locations. These results offer some perspective to the fate and effects of other pollutants that may be added to Georges Bank in the future. If the pollutant is rendered harmless by dilution, then the environmental concern is minimized. On the other hand, if the pollutant is dangerous at any concentration, then the problem may intensify because the same energetic processes will disperse the pollutant and quickly endanger a wide area of the bank.

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34. Geochemical Studies of Plants and Soils in the Beluga Coal Field, Alaska

By R.C. Severson *and* Larry P. Gough

Evaluation of the geochemistry of undisturbed plants and soils is essential for objective predictions of the rehabilitation potential of an area to be disturbed by strip mining. These data also can be used after mining and rehabilitation to monitor geochemical changes in the landscape resulting from the rearrangement of rock strata and the disruption of soil development and of natural plant communities.

A predevelopmental geochemical survey was conducted for the Capps area of the Beluga coal field (fig. 34.1; table 34.1). Soil and plant collections were conducted according to an analysis-of-variance sampling design. This design allowed us to (1) determine the appropriate scale for geochemical mapping, (2) estimate the minimum number of samples necessary to prepare stable map patterns, and (3) establish geochemical baselines. The data were also used to examine the relations between soil geochemistry and plant uptake. Details of the methods used and results obtained are given in Severson and Gough (1983, 1984) and Gough and Severson (1983). A summary of these results is presented here.

Stable geochemical maps were prepared, on the basis of mean element content within a 1-km^2 cell, for pH and total levels of Al, Cu, Fe, Mg, P, Sr, and V and for diethylenetriamine pentaacetic acid- (DTPA-) extractable levels of Cu, Mn, P, and Zn in surface soil zones. Stable geochemical maps were also prepared for plant materials: willow (Al, As, B, Ca, Cu, Fe, K, La, Ni, P, S, and Sr) and

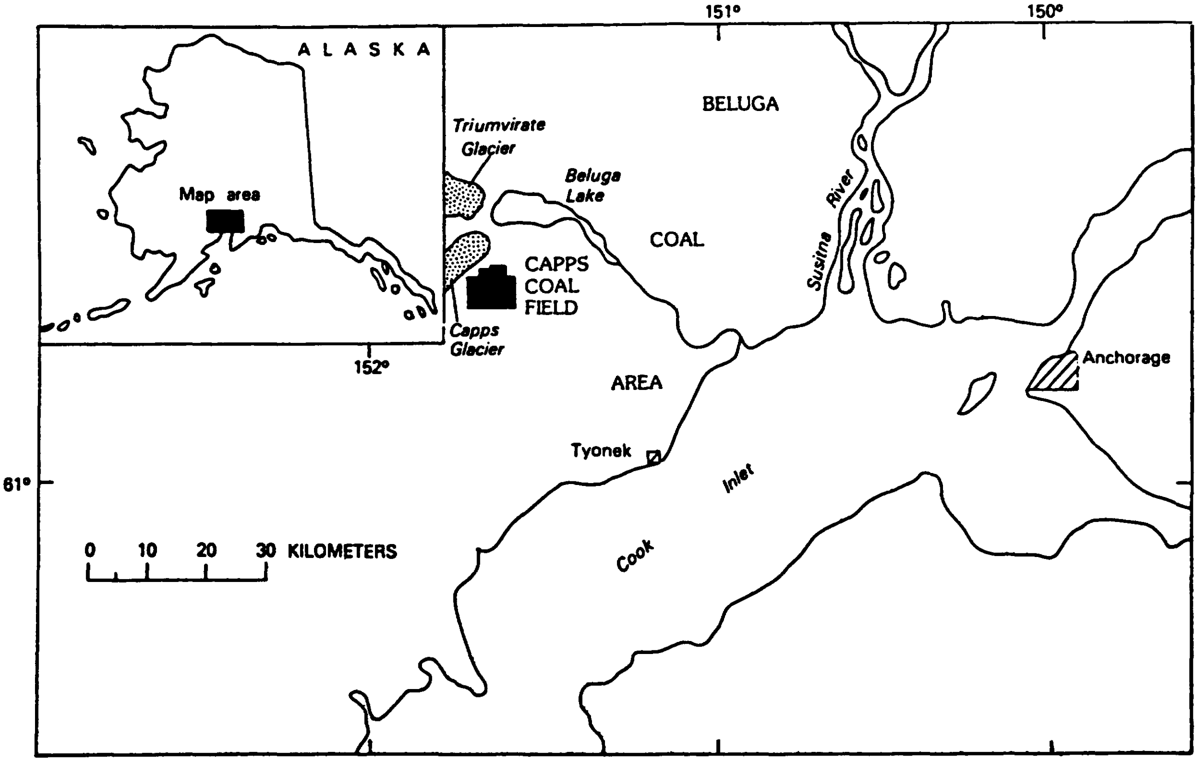

Figure 34.1. Location of the Capps coal field, Alaska.

Table 34.1. Observed range in concentration (in parts per million unless otherwise indicated) of six elements in samples of two soil zones and three plant species (dry weight basis) from the Capps coal field, Alaska

[*n*, number of samples]

Sample	Aluminum	Copper	Iron	Manganese	Phosphorus	Zinc
AB-DTPA[1] soil extract						
Upper zone (*n*=90)	19–240	1.9–9.3	160–560	3.8–64	6–60	0.5–8.2
Lower zone (*n*=90)	32–760	1.1–15	140–750	0.7–21	7–50	0.5–6.9
Total content in soil						
Upper zone (*n*=90)	7.2–10%	22–7	3.8–5.9%	860–1,300	70–110	61–98
Lower zone (*n*=90)	4.0–9.5%	11–120	1.3–18%	220–2,800	30–1,500	30–110
Calamagrostis canadensis (*n*=26)	<16–36	5–15	16–84	200–720	0.16–0.52%	29–72
Festuca altaica (*n*=64)	<16–400	3.1–13	16–260	170–690	0.19–0.45%	4.7–80
Salix pulchra (*n*=90)	16–220	2.1–12	16–130	52–340	0.072–0.33%	48–120

[1] AB-DTPA, ammonium bicarbonate-diethylenetriamine pentaacetic acid.

grass (As, B, Ba, Ca, Cu, Mg, Na, and S). The map patterns suggest relative independence of soil geochemistry to that of the plants; however, DTPA-extractable soil-element levels correspond better with plant chemistry than do total soil-element levels. Geochemical baseline data for soils and plants suggest that these compositions are not unusual when compared with geochemical baseline data from other natural areas.

Table 34.1 lists the observed range in concentration of six biologically important elements as determined in a soil extract, in a total digestion of soil, and in the dry material of three plant species. The extractable and total concentrations measured in the soil are assumed to represent physiologically acceptable ranges within which the normal growth of these three species takes place. These soil-concentration ranges, therefore, may be used in judging the feasibility of revegetating areas disturbed by mining and similar operations when native vegetation is to be used in site rehabilitation. The range of element concentrations in plant materials is also a measure of physiological tolerance. Additional work is needed, however, to determine if soil-extractable levels are a good measure of element availability for the uptake and translocation of these elements in these plants.

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35. Potential Saltwater Intrusion into Freshwater Aquifers During Exploration for and Mining of Phosphorite off the Southeastern United States

By Frank T. Manheim

Studies in the 1980's (Riggs, 1984) demonstrated the seaward extension of major phosphorite resources off the North Carolina coast in Onslow Bay; similar extensions off South Carolina, Georgia, and Florida are possible. Evaluation and development of this resource present a possible hazard to freshwater aquifers.

New slurry mining technology promises to extend mining of phosphorite to depths as great as 100 m beneath the sea floor. On the basis of current stratigraphic information and the new technology, some experts predict that the Atlantic margin from North Carolina to Florida will prove to contain the largest mineable phosphorite resource in the world. The new slurry mining technique not only permits mining of deeper deposits but also permits tailings and other wastes to be deposited within the caverns that are left after the ore is recovered. The technique creates less turbidity and fewer other environmental effects than do alternative mining methods, such as dredging. The possibility of offshore mining may be enhanced by the fact that the opening of new mines in the Florida phosphate fields has virtually ceased as a result of environmental or local opposition.

Exploration drilling and drilling associated with the phosphorite development will result in invasion by seawater of buried deposits that are the seaward extension of freshwater aquifers. This invasion may adversely affect offshore freshwater-bearing strata that serve as buffer zones against saline-water encroachment into land aquifers. These freshwater-bearing offshore strata first became known in the late 1960's as a result of the Joint Oceanographic Institutions Deep Earth Sampling Project (JOIDES) drilling off Florida. Studies showed that fresh and brackish ground waters are not limited to the Florida Peninsula but extend as far as 120 km from shore or to the edge of the shelf (Manheim and Horn, 1968; Manheim and Paull, 1981) (figs. 35.1 and 35.2). The U.S. Geological Survey (USGS) Atlantic Margin Coring Project (AMCOR) drill holes in 1976 revealed that a freshwater to brackish-water tongue extended underneath the entire Atlantic shelf (Hathaway and others, 1979; Kohout and others, 1988). Unpublished studies by S.R. Riggs and F.T. Manheim (data on file at USGS offices in Woods Hole, Mass.) show that near-potable water can be found even near the base of 6-m-long vibracores in Onslow Bay. This distribution of freshwater is linked with freshwater recharge during the exposure of the continental shelf during the Pleistocene glacial maximum. Freshwater lenses shield coastal ground-water resources from saline encroachment and are thus of great importance to coastal cities, such as Savannah, Ga., that rely upon ground water for their water supply.

The nature and distribution of the offshore freshwater lenses in most areas are still poorly known and defined.

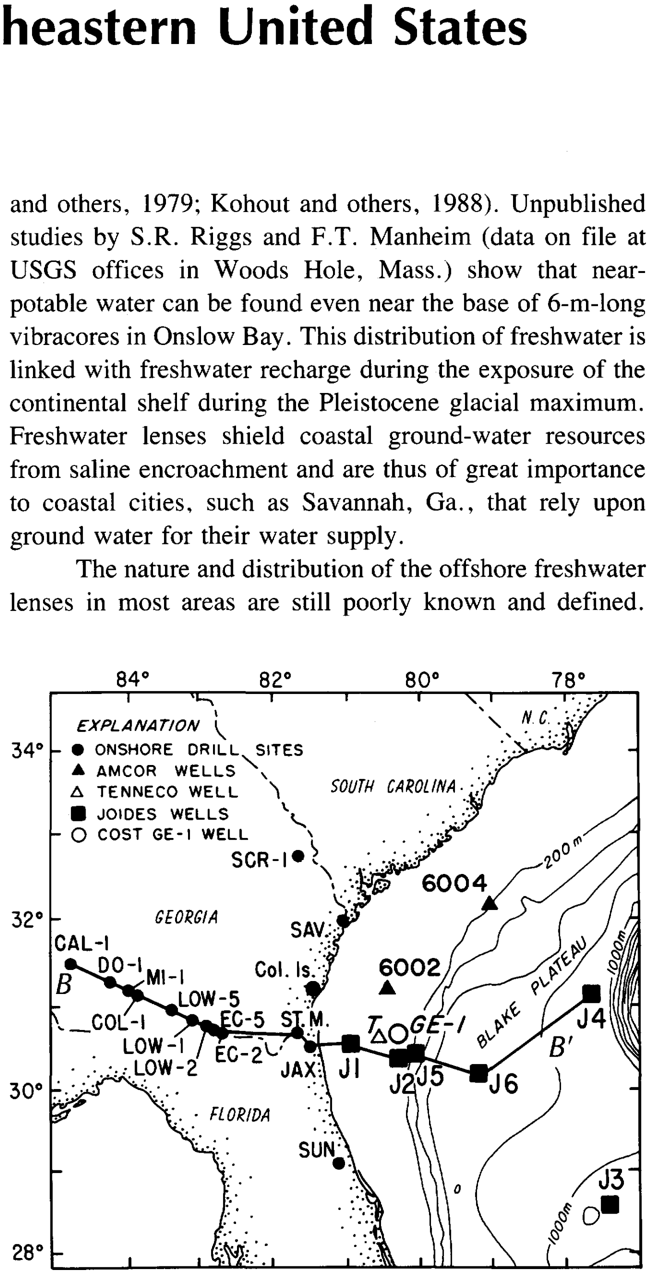

Figure 35.1. Location of hydrochemical transect *B–B'*, from Georgia to the Blake Plateau. COST, Continental Offshore Stratigraphic Test; JOIDES, Joint Oceanographic Institute's Deep Earth Sampling; AMCOR, Atlantic Margin Coring Project. From Manheim and Paull (1981). Base map modified from Uchupi (1968).

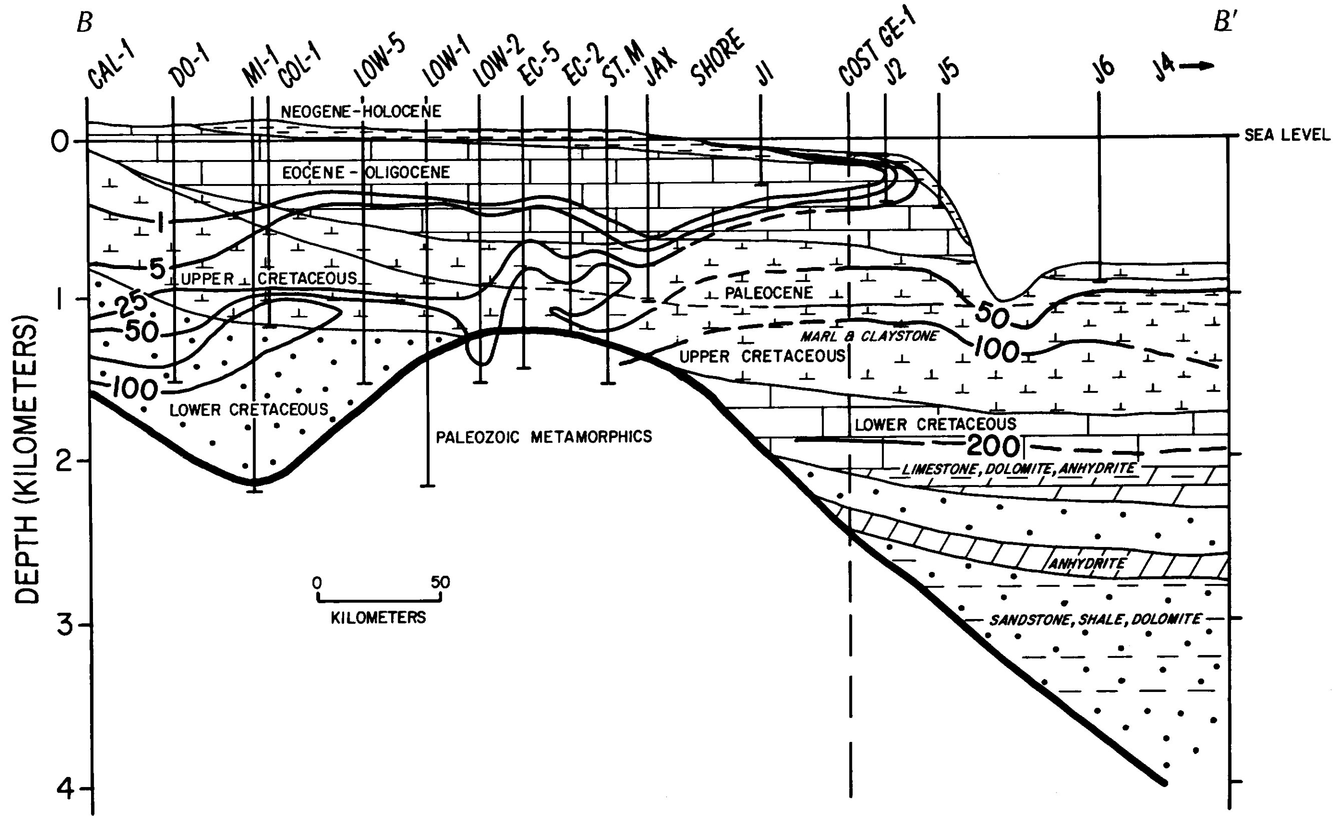

Figure 35.2. Hydrochemical transect *B–B'* from land (Georgia) to Blake Plateau. Location of transect is indicated on figure 35.1. Salinity contours are in grams per kilogram; dashed where inferred. Vertical lines refer to drill holes identified and discussed in Manheim and Paull (1981).

They will require detailed examination and modeling in conjunction with offshore exploration and exploitation of potential mineral resources. Studies should be timed so that hydrologic models will be in place by the time leasing occurs.

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36. Some Basic Facts About Radioactive Radon

By Joseph S. Duval *and* Allan B. Tanner

Radioactive radon (^{222}Rn) is produced naturally in most rocks and soils as part of the radioactive decay series of ^{238}U (fig. 36.1). ^{222}Rn has a half-life of 3.823 days and can move significant distances from the site where it was produced. It can move about 1 m by diffusion in fractured rocks and permeable soils, and convection resulting from water or gas flow may increase the distance to 5 m or more. Radon can enter a house in a variety of ways (fig. 36.2).

Once radon enters a house, it ultimately decays to produce three alpha-particle-emitting isotopes of polonium (see fig. 36.1). These alpha particles have been identified as an important cause of lung cancer when exposure levels were significant (National Council on Radiation Protection and Measurements (NCRPM), 1984). The unit of measure used to define exposure to radon daughter isotopes is the Working Level Month (WLM), which is defined as exposure to an average of 1 Working Level (WL) for a working month of 170 hours. WL is defined as a concentration of radon daughter isotopes that have a potential alpha energy release of 130,000 MeV (million electron volts) per liter of air. The exposure level can be estimated by a direct measurement of radon, and a radon concentration level of 200 picocuries per liter (pCi/L) is approximately equivalent to 1 WL. The health risk of exposure to radon can be expressed as the number of excess lung cancer deaths in persons exposed to a particular level. NCRPM (1984) estimates that 0.91 percent of people exposed to 1 WLM per year during their lifetime will die of lung cancer but that the effects of an exposure level of 0.2 WLM per year are minimal. This latter level implies that radon daughter concentrations equivalent to 0.004 WL can be considered safe for continuous, 24-hours-per-day exposure. The level currently being used as a guideline by the Environmental Protection Agency at remedial action sites is 0.02 WL (approximately 4 pCi/L of radon).

The problem of defining and estimating the indoor radon hazard potential (*H*) can be expressed as the product of two functions:

$$H=G\times C$$

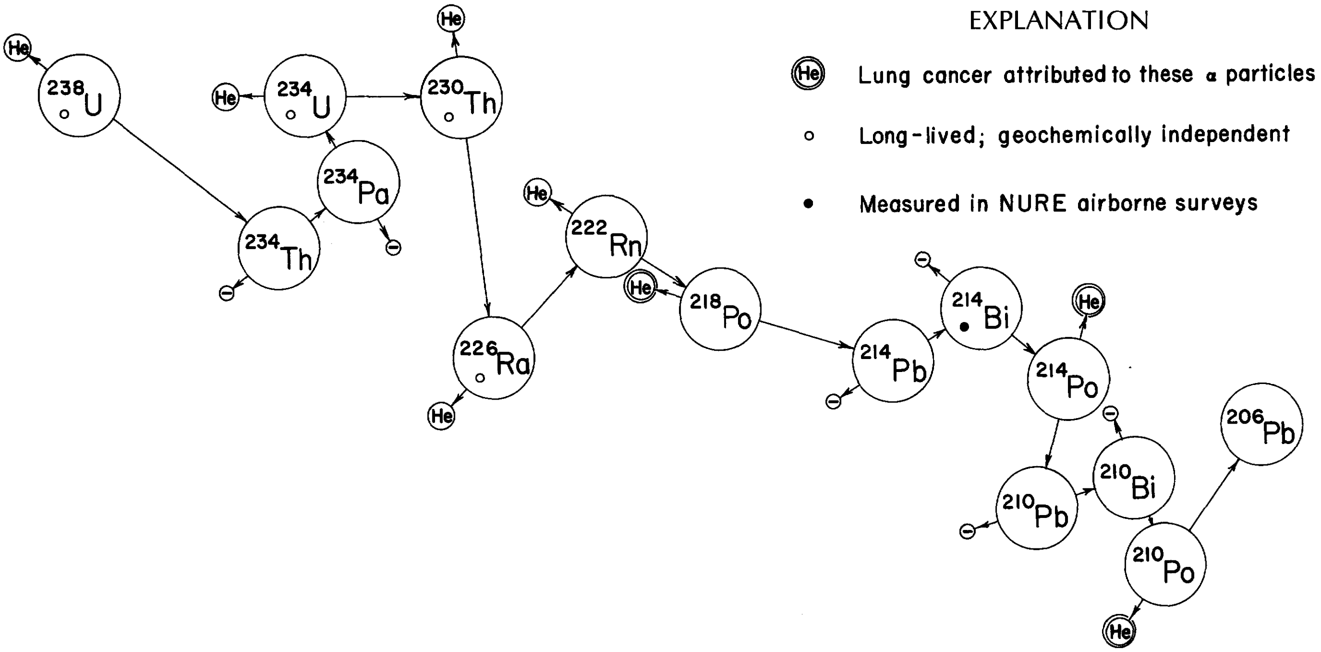

Figure 36.1. ^{238}U decay series. NURE, National Uranium Resource Evaluation.

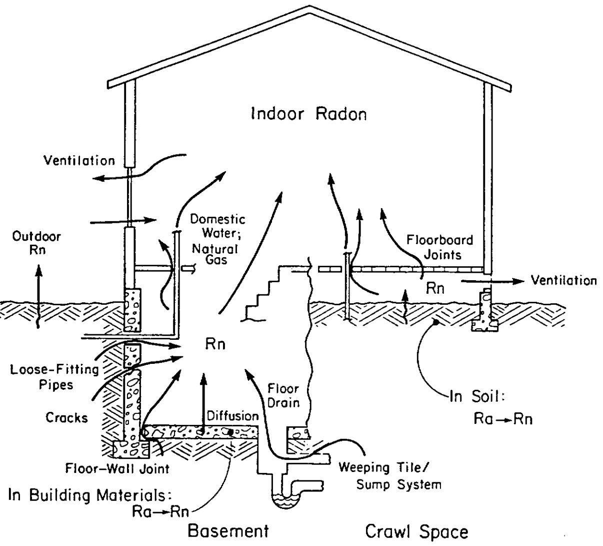

Figure 36.2. Common paths of entry of radon into homes (from Sextro, 1985).

where *G* is a geologic function that defines those parameters that control the availability of radon in the soil gas (see Otton, this volume) and *C* is a building-construction function that defines the parameters that control the entry of radon into a house. The form of these functions is presently unknown, and extensive research is being done to define them. The geologic function must include such parameters as the total radon in the soil gas, the total radon production rate, the emanating power of the geologic materials (the fraction of the total radon produced in the host materials that escapes into the soil gas), permeability, soil moisture, and convection resulting from gas or water flow. The total radon in the soil gas can be measured by suitable soil gas measurement techniques. The total radon production rate can be directly measured by using gamma-ray spectrometric techniques. The emanation power can also be directly measured in the laboratory, and field techniques can be developed. Permeability, soil moisture, and diffusion coefficients can be measured as well, but convection effects will be difficult to assess. The relative importance of the geologic parameters are not known and will require separate assessments. Existing data on indoor radon levels suggest that (1) high radium (parent of radon, fig. 36.1) concentrations result in high radon hazard potential, (2) normal radium concentrations and emanating power coupled with high porosity and permeability produce a high radon hazard potential, and (3) low porosity or water saturation results in low radon hazard potential. The construction function must include the effective permeability of the house (see fig. 36.2) and the pressure differences across building-soil interfaces. Ventilation and barrier techniques have been shown to be effective in reducing the indoor radon concentration levels.

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37. Geology of the Reading Prong, New York, and Its Application to Predicting Areas That Have High Radon Potential

By Linda C. Gundersen

Geologic and metallogenic models for uranium occurrences in the Reading Prong (Grauch, 1978; Gundersen, 1984, 1986) can be used to predict source areas for radon gas. Recent testing in Pennsylvania, New Jersey, and New York indicates that geologic factors strongly control the distribution of radon in homes and water supplies. Specifically, fault zones, highly uraniferous rocks, and uranium occurrences commonly associated with magnetite appear to be the major geologic influence.

Some recently discovered elevated levels of radon in water supplies and in homes built on the Reading Prong illustrate the influence of geology on radon migration and accumulation. In Pennsylvania, one of the highest levels of radon gas ever recorded in a residential building was measured near Boyertown. The home was built directly on weathered Proterozoic bedrock over a uranium-rich shear zone. Radioactive decay of uranium was the most likely source for the radon, and the high transmissivity of the fault and high permeability of the weathered bedrock favored radon mobility. Elevated levels of radon in water have recently been discovered in Warwick, N.Y. Well water in this area comes from fractures in the Proterozoic rocks. Warwick has the largest radiometric anomaly on the National Uranium Resource Evaluation (NURE) aerial gamma-ray map of the Reading Prong (LKB Resources, Inc., 1980) and is known for its highly uraniferous magnetite deposits. In Fort Montgomery, N.Y., the soils are high in uranium and radon. Fort Montgomery is located on both a magnetic and a radiometric high and is the former site of one of the largest iron mines in New York. Uranium-rich material from the old magnetite mine probably caused the high uranium and radon in the soil.

The Reading Prong physiographic province is composed of three subprovinces known as the Hudson Highlands in New York, the New Jersey Highlands in New Jersey, and the Reading Hills in Pennsylvania. The Proterozoic rocks underlying the Reading Prong are a sequence of volcanics and sediments that were metamorphosed during the Grenville orogeny (approximately 1 billion years ago) and syntectonically intruded by granites of different compositions. Parts of the Reading Prong were refolded during the Paleozoic. Systematic faulting and jointing occurred regionally during the Proterozoic, Paleozoic, and Mesozoic Eras. Recent geological investigations (Helenek, 1971; Drake, 1984; Gundersen, 1985) have divided the Proterozoic rocks into distinct groups that are recognizable throughout the Reading Prong. They consist from bottom to top of the following stratigraphic units: (1) a calc-silicate gneiss, consisting of a basal hornblende amphibolite and pyroxene gneiss and minor quartz-feldspar gneiss, marble, and allanite- and scapolite-bearing gneisses; (2) a quartz-oligoclase leucogneiss and minor hornblende and pyroxene amphibolite; (3) a hornblende gneiss; and (4) a predominantly metasedimentary sequence consisting of graphitic quartz-feldspar gneiss, graphitic biotite gneiss, biotite-garnet gneiss, and minor hornblende-feldspar gneiss, marble, and pyroxene gneiss. Pegmatites are ubiquitous in all the rocks and are the product of local anatexis. Leucogranite and hornblende granite locally intrude this sequence, and in the Hudson Highlands and the Reading Hills they constitute a significant part of the bedrock. A major Proterozoic marble belt, known as the Franklin Marble, extends along the western flank of the New Jersey Highlands and into easternmost Pennsylvania.

Magnetite deposits, from which iron was produced in the 18th and 19th centuries, form concordant layers within the calc-silicate gneiss and hornblende gneiss in New York and New Jersey. In Pennsylvania and parts of New Jersey, magnetite deposits also occur in amphibolitic layers in the quartz-oligoclase leucogneiss and in the graphitic biotite gneiss. Iron- and copper-sulfide, uranium, thorium, phosphate, and rare-earth elements are associated locally with the magnetite deposits. Mining and exploration for uranium took place in the 1950's through the 1970's.

Uranium, most commonly in the form of the mineral uraninite, occurs in three general host-rock associations: (1) magnetite-rich zones and deposits within the gneiss and associated faults and fractures; (2) granitic intrusives and

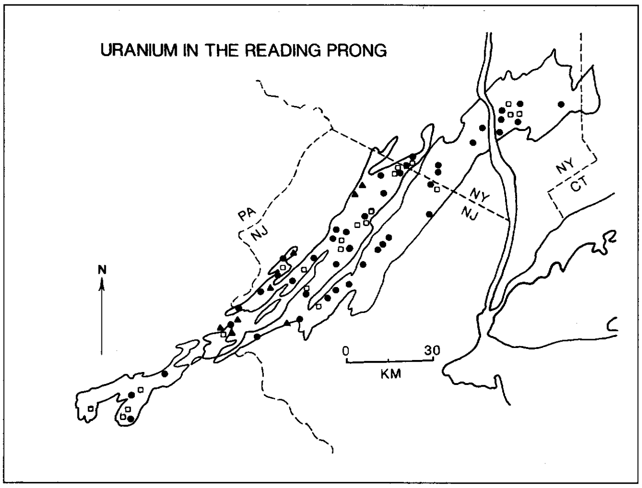

Figure 37.1. Location of known uranium deposits in the Reading Prong. Closed circles represent magnetite-associated uranium, open squares represent uranium hosted in granitic gneiss or pegmatite, and closed triangles represent uranium hosted in marble.

pegmatites; and (3) marble (Grauch and Zarinski, 1976; Bell, 1983; Gundersen, 1984, 1986). In southern New York and northern New Jersey, the magnetite-associated uranium is the predominant type of show (fig. 37.1). Rocks that are high in iron also tend to be high in uranium (fig. 37.2). In Pennsylvania, uranium occurs in magnetite-bearing zones, magnetite mines, serpentine deposits within the Franklin Marble, granite gneiss, and graphitic gneiss.

The rock sequence (units 1–4 above) and mineral deposits just described may have originally been deposited in a Proterozoic marginal-marine basin as (1) mafic to intermediate volcanics, carbonate sediments, and exhalative iron-, sulfide-, and uranium-rich horizons; (2) silicic volcanics; (3) mafic volcanics and exhalative iron-, sulfide-, and uranium-rich horizons; and (4) silicic volcaniclastics, carbonaceous pelitic sediments, carbonate sediments, and minor exhalative iron-, sulfide-, and uranium-rich horizons. Similar sequences and mineral deposits are found in the Precambrian rocks of Canada, the northern midcontinent and East Coast of the United States, and in Australia, Scandinavia, China, and India. Many anorthosite-related extensional basin sequences, such as those that flank the Adirondacks, also host magnetite-associated uranium occurrences. In general, it appears that these types of deposits occur most frequently in marginal and cratonic extensional basins, usually of Precambrian age (Hauck and Kendall, 1984).

The geologic and metallogenic model presented here can be used in the preliminary assessment of the Reading Prong to predict areas that have high radon potential. Quartz-oligoclase leucogneiss usually contains small amounts of uranium, whereas quartz-feldspar gneiss and granite have larger amounts of uranium. Magnetite ore, pyroxene gneiss, hornblende gneiss, pyroxene amphibolite, and graphitic biotite gneiss, especially those containing large amounts of iron, tend to have the highest uranium content. Uranium is also found in higher concentrations along the contacts between gneiss and granite intrusives and pegmatites. Major faults and fault junctions in the uraniferous gneisses and marbles are commonly mineralized with uranium and provide a conduit for the radon gas. Unconsolidated surficial materials, such as soil, alluvium, and glacial till, play a major role in radon transport from bedrock and fault sources into the foundations of buildings. Highly permeable surficial deposits increase the potential for high levels of radon accumulation. In New Jersey, much of the glacial till is derived from the underlying bedrock and may also serve as a source of radon. Current studies in the Reading Prong include the development of preliminary maps of radon potential based on bedrock geology, surficial geology, location of major fault zones, chemical and geophysical data, and geologic and metallogenic models for uranium. Future studies proposed for the Reading Prong include field measurements of radon migration through different types of soil and glacial deposits, the effects of permeability and moisture content on radon migration, the behavior of radon around faults, and the relation of the physical properties of bedrock and surficial materials to the amount of radon in the soil and homes.

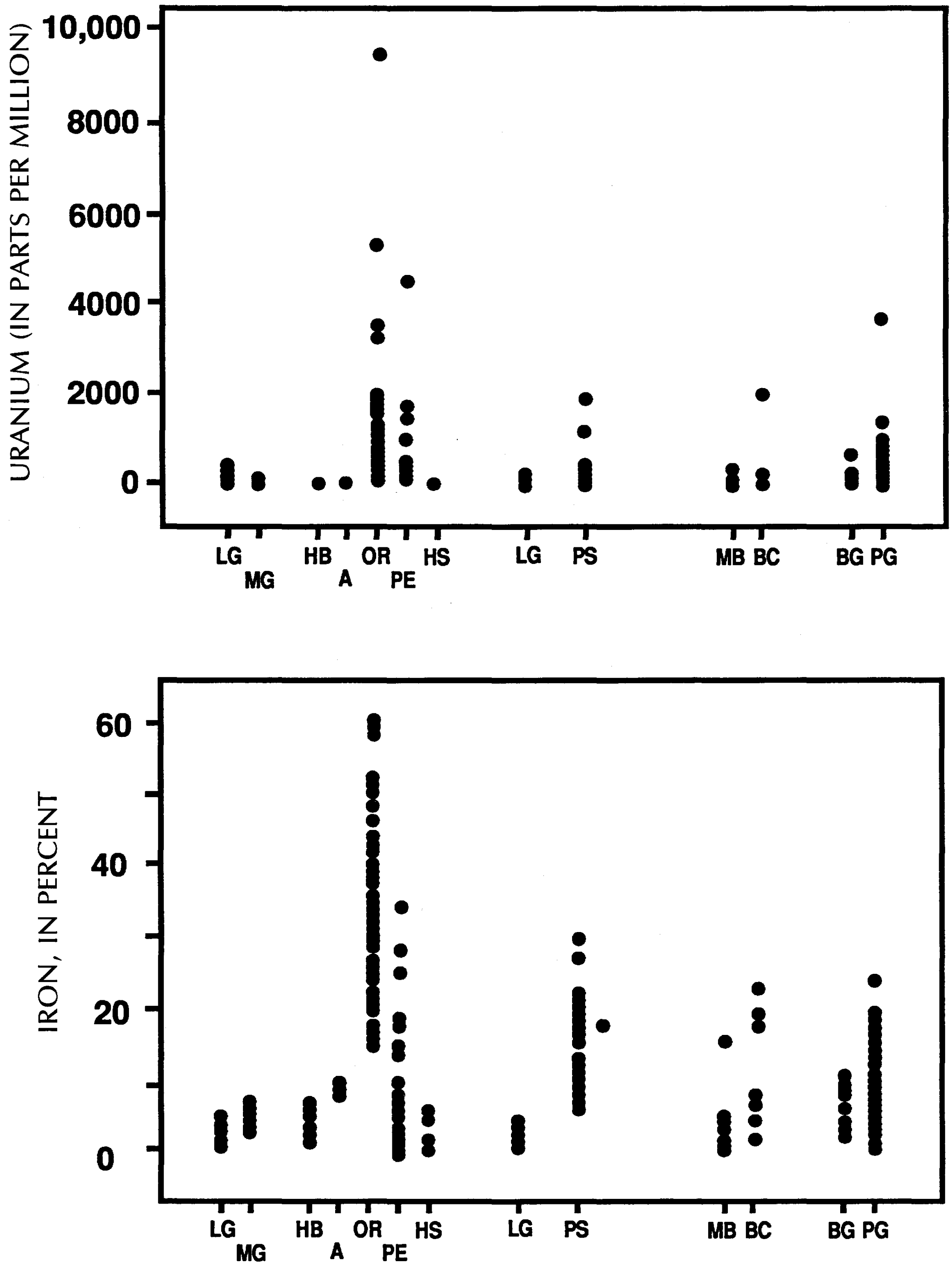

Figure 37.2. Uranium in parts per million (ppm) and iron in percent versus rock type for metamorphic rocks from the Reading Prong, Greenwood Lake quadrangle, New York and New Jersey. Rock types from left to right are quartz-oligoclase leucogneiss (LG), melanocratic pyroxene gneiss (MG), hornblende gneiss (HB), amphibolite (A), magnetite ore (OR), pegmatite (PE), hornblende gneiss having high iron and copper-sulfide content (HS), pyroxene leucogneiss (LG), pyroxene gneiss and pyroxene amphibolite having high iron and copper sulfide content (PS), marble (MB), brecciated pyroxene gneiss (BC), biotite gneiss (BG), and pyroxene gneiss having abundant magnetite (PG).

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38. The Role of National Uranium Resource Evaluation Aerial Gamma-Ray Data in Assessment of Radon Hazard Potential

By Joseph S. Duval

National Uranium Resources Evaluation (NURE) aerial gamma-ray surveys measure the intensity of natural gamma rays emitted by members of the radioactive decay series of uranium, potassium, and thorium. The data from these surveys may be useful in trying to assess the hazard of radon in homes. In the uranium decay series, one of the daughter products is the radioactive gas radon (^{222}Rn). ^{226}Ra, the last long-lived member of the series, has a half-life of 1,602 years (fig. 38.1). Radon has a half-life of 3.823 days, which is short in geologic terms but is long enough to allow the gas to move significant distances from the point of origin if the host rock and (or) soil has high gas permeability. In soils, gas diffusion calculations (Tanner, 1964; Fleischer and Likes, 1979) suggest that, prior to decaying, the radon can move distances of about 1 m or less; however, convection resulting from gas or water flow may increase the distances to 5 m or more in porous or fractured earth materials. The daughter products following radon (fig. 38.1) have half-lives ranging from 3.05 to 26.8 minutes. One of these, ^{214}Bi, produces the gamma rays that are measured by the aerial gamma-ray system. Because their short half-lives prevent the daughter products, including radon, from traveling far from their parent in rocks or soils, the aerial gamma-ray surveys provide a direct measurement of the amount of radon produced in the near-surface materials. These data do not, however, provide any direct information about how much of the radon produced is not retained in the host materials but is in the soil gas and free to move.

Aerial gamma-ray measurements represent averages of the near-surface concentrations of radon. The materials that contribute more than 80 percent to the aerial measurement include the rock and soil to a depth of about 30 cm over a circular area that has a radius approximately equal to twice the altitude of the aircraft (Duval and others, 1971). The surface area included in the average varies as a function of the height of the gamma-ray detector above the ground surface (fig. 38.2). Many aerial gamma-ray surveys are flown approximately 400 feet above the ground. This was true for the surveys flown as part of the U.S. Department of Energy NURE Program. The percentage of the surface area actually measured by a survey is a function of the

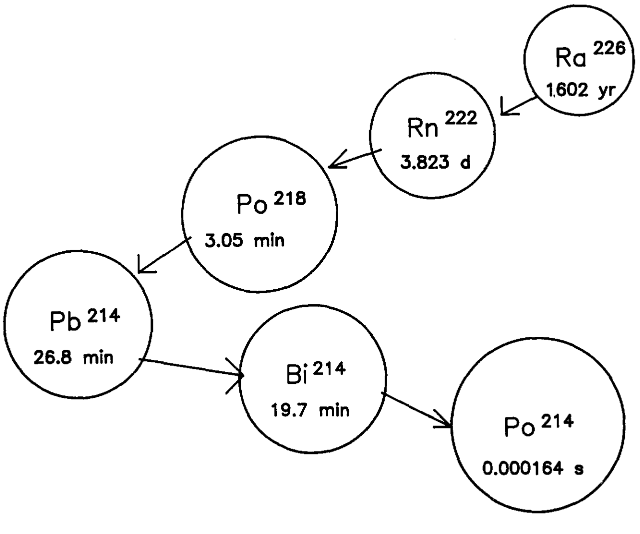

Figure 38.1. Portion of ^{238}U decay series.

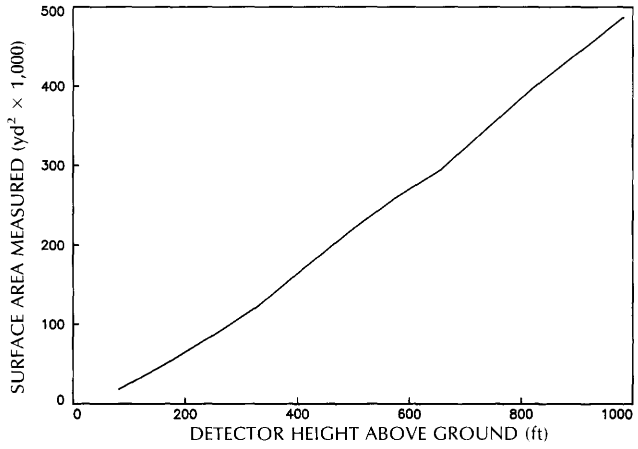

Figure 38.2. Surface area measured as a function of the height of the detector.

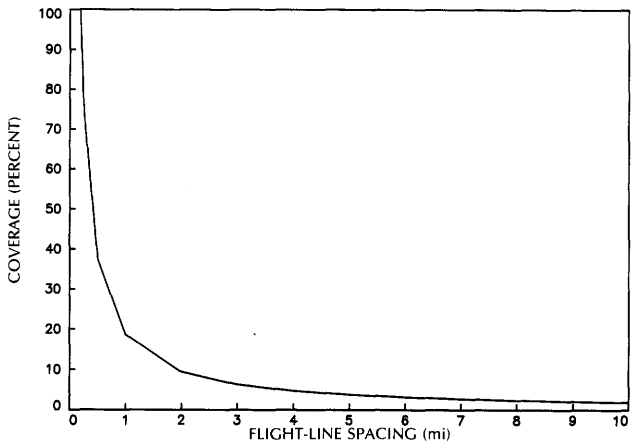

Figure 38.3. Percentage of surface area covered versus the flight-line spacing.

flight-line spacing used (fig. 38.3). Because most of the NURE surveys had flight-line spacing of 3 or 6 miles, they provide data for less than 10 percent of the surface area. Although this amount of coverage is not sufficient for extensive site-specific assessments, the data can be used to generate regional-scale maps and to provide site-specific information along the flight lines.

The NURE data can be presented in the form of contour maps or flight-line profiles of the near-surface equivalent uranium (eU), potassium (K), and equivalent thorium (eTh) concentrations. The term "equivalent," denoted by the lowercase "e," emphasizes that both the uranium and thorium decay series have a potential for radioactive disequilibrium caused by differences in chemical behavior among the various daughter nuclides. These maps and profiles can be used to identify areas where the uranium concentrations are relatively high; however, they provide no indication of the radon emanation power of the materials, which is a measure of the ratio of the radon in the soil gas to the total amount of radon produced. Duval (1983) developed a technique that combines the uranium concentration data with the eU:K and eU:eTh to produce composite-color uranium maps. The assumption used to interpret these maps is that high values of all three parameters (eU, eU:K, and eU:eTh) indicate that uranium concentration has occurred. If the uranium has been concentrated by metamorphic, igneous, hydrothermal, or low-temperature aqueous processes, the radon hazard potential may be enhanced. The concentration maps, profiles, and composite-color maps can be used to provide an initial classification of the surface rock and soil regarding radon hazard potential. This classification will have to be modified and improved by using geologic data and measurements of the radon concentrations in soil gas.

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39. Potential for Indoor Radon Hazards—A First Geologic Estimate

By James K. Otton

INTRODUCTION

Two principal factors that determine the level of radon in a dwelling are (1) the availability of radon in the ground and (2) the structural characteristics of the dwelling. Of these, only the availability factor is a function of the natural environment and is the only one considered here. Although high radon levels in specific buildings may be caused by the use of uranium-rich and radium-rich natural building materials or by the degassing of radon-rich waters in showers and other devices in the home, the principal natural source of indoor radon is soil gas that moves into the dwelling through the foundation by diffusion or by flow caused by air-pressure differences. Subjacent bedrock is usually a major contributor of radon also, especially where soils are thin or where the bedrock is uranium or radium enriched and permeable. The availability of radon in soil gas is dependent on the radium concentration in the soil and bedrock, the emanating power of the soil (that fraction of the radium in mineral grains that produces radon in soil pores), the soil porosity and permeability, and the moisture content of the soils.

The radium content of soils and bedrock is a result of a series of complex water and rock interactions in the uranium geochemical cycle that involves leaching of uranium and its daughter products from their sources, transport of these elements in surface and ground waters, and fixation of the elements in a host. Radon is the product of a decay chain of geochemically distinctive radioelements. Most of the radioelements in that chain are cations soluble in and largely transported by water, but radon is an inert gas that can be transported by either water or air.

Because a radon problem starts with radon's availability in the ground, an understanding of the geology and geochemistry of uranium and radium and an understanding of the geology and physical properties of soils should make it possible to predict where radon hazards may occur. However, the interplay between radium concentrations in soils and subjacent bedrock and the porosity and permeability of the soils, although critical, has been little studied. Case studies do suggest, however, that high concentrations of uranium and radium in soils and subjacent bedrock can cause severe radon problems (greater than 1 Working Level (1 WL) or 200 picocuries per liter (pCi/L)) in indoor air no matter what the soil characteristics. High concentrations of uranium in bedrock are the causes of the highly publicized radon hazards in residences in the Boyertown, Pa., area of the Reading Prong (Robert Smith, written commun., 1986) and in residences built over certain granites and most alum shales in Sweden (Akerblom and others, 1984). However, highly porous and permeable soils can cause elevated radon concentrations (0.1 to 1 WL or 20 to 200 pCi/L) even if the uranium and radium concentrations in a soil are only average, simply because large volumes of soil gas may move into buildings through permeable soils. For example, houses constructed on glacial outwash gravels and eskers have been documented as having high levels of indoor radon in some areas of the United States and in many areas of Sweden. Conversely, heavy clay soils and sediments, especially where water saturated, can nearly block all soil-gas migration.

GEOLOGIC SITUATIONS THAT MAY PRODUCE ELEVATED INDOOR RADON LEVELS

The existing information on uranium and radium geology and geochemistry, including the National Uranium Resource Evaluation (NURE) aeroradiometric data (J.S. Duval, written commun., 1986), and studies of radon soil gas and indoor radon strongly suggest that terrane overlying uranium occurrences has the highest probability of producing severe radon levels in indoor air (greater than 1 WL or 200 pCi/L). These data also show that certain rock types are known to contain uranium concentrations above the average for most rocks. These rock types are likely to contain elevated radon concentrations in soils and weathered bedrock across their outcrop area but are not likely to produce severe levels. In some cases, unusually high permeability of the underlying rocks increases the radon hazard potential. On the basis of present information, the geologic terranes listed below are believed to have an increased likelihood for producing significantly elevated radon concentrations in homes.

Granitic and Metamorphic Terranes

Example A. The Reading Prong of Pennsylvania, New York, New Jersey, and Connecticut.—Anomalously uraniferous Proterozoic? metamorphic rocks and local uranium occurrences of the Reading Prong have produced high average levels and locally severe radon levels in some homes in Pennsylvania. The national index home for radon (13 WL) is located in this province near Boyertown, Pa. Geologically similar terranes exist elsewhere in the Eastern United States (Grauch and Zarinski, 1976), but these other areas are largely unevaluated.

Example B. Glaciated Paleozoic granitic and high-grade metamorphic terranes in Maine and New Hampshire.—Radon problems in ground waters associated with anomalously uraniferous granites and high-grade metamorphic terranes were initially identified in Maine (Brutsaert and others, 1981) and New Hampshire (F. Hall, University of New Hampshire, oral commun., 1986). Subsequently, elevated indoor-air radon concentrations were identified in Maine (M. Lanctot, Maine Geological Survey, oral commun., 1986). Similar areas exist throughout the Eastern United States, but many of them are not glaciated and instead are deeply weathered. The effects of deep weathering on radium geochemistry and radon movement in soils need to be evaluated.

Phosphate Lands

Reclaimed phosphate mining areas in Florida were recognized in early studies as radon problem areas. Subsequent work has shown that unmined phosphate lands in these same areas have similar if not higher radon levels in homes (Florida Department of Health and Rehabilitative Services, 1978). Phosphate lands exist elsewhere in the United States but have been less thoroughly evaluated for radon problems.

Pleistocene and Holocene Glacial Outwash Gravels

These sediments are unusually permeable and form soils that also are unusually permeable. Elevated levels of radon are common in the east Spokane, Wash., and the northern Idaho areas that are underlain by such gravels, especially where the gravels are derived from granitic rocks. Locally, radon values in houses may approach severe levels (Lawrence Berkeley Laboratory, written commun., 1986).

Glacial Till and Moraine, Loess, and Lacustrine Clay

Although these sediments are generally poorly sorted and low in permeability, they are locally highly permeable or are locally very fine grained and have high radon-emanating power. Thus, even though they are not always high in uranium or radium concentrations, soils over these sediments may have high radon availability. Radon levels can be elevated where these sediments are derived from uraniferous rocks such as granites or marine shales. A few indoor and soil-gas radon studies over these sediments in the North-Central States suggest locally high values for radon (see, for example, the newspaper Fargo Forum, Oct. 20, 1985).

Carbonate Terranes, Especially Karst Cave Areas

Caverns and caves in the National Park Service system have been evaluated for radon hazards, and a significant number of them have hazardous levels of radon (Yarborough, 1980). Some caves contain several working levels of radon. Although limestones and dolomites generally do not contain elevated levels of uranium or radium, they commonly contain phosphatic material, lenses of carbonaceous mudstone, or volcanic ash. Uranium contents are higher where these other materials are present. In addition, the clays and iron oxyhydroxides that form the principal weathering products of limestones and dolomites are very effective adsorbents of uranium and radium. The high permeability of weathered limestones and the fine grain size of these weathering products also make them very efficient radon emitters. The few studies of indoor air and soil gas that have been conducted in carbonate terranes suggest that a significant percentage of the values are elevated (Sachs and others, 1982), and possibly some are locally severely elevated. Carbonate rocks are found over wide areas of the Central and Eastern United States.

Marine Black Shales, Especially Devonian Shales of the Central United States

These rocks have long been known for their elevated uranium concentrations. One study of soil gas and indoor air in part of New York State suggests that elevated radon concentrations exist over these rocks (Lilley, 1985). Similar, although more uraniferous, rocks in Sweden have been identified as a major radon hazard (Akerblom and others, 1984). Again, marine black shales are widely distributed and underlie parts of major population centers, especially in the Central United States. Other types of marine shales, for example, the Pierre Shale of the Western United States, contain slightly elevated uranium concentrations and may create some radon hazards.

Arkosic and Volcaniclastic Alluvial Conglomerates and Sandstones

Such rocks exist in several areas of the country in terranes that range from Proterozoic? to Holocene age. Areas in which uranium concentrations are known to be elevated include parts of basins adjacent to the Front Range of Colorado, parts of the Mesozoic basins of the Eastern United States, the areas underlain by the Ogallala and White River Formations of the High Plains of Texas, Nebraska, and elsewhere, and many intermontane basins in the Western United States, notably in Wyoming and Montana. Many of these units host uranium occurrences and deposits. Locally, radon levels may be more severe in homes near uranium occurrences, and generally there may be elevated radon values. A few studies of uranium in waters and of radon in waters, soil gas, and indoor air in some of these areas suggest that concentrations of radon significantly above the national norm may be expected.

CONCLUSIONS

This list must be regarded as only a first compilation. It must be emphasized that not every building over one of these rock types has elevated radon levels. Many sources of variability affect radon levels in bedrock, soil gases, and inside structures. For example, granites vary in their uranium content. Considerable variability is attributable to housing factors. Much work is required on each of these types of terranes, as well as on other terranes, to establish whether radon hazards exist and, if they do, to determine their extent and their causes. Other rock types may also produce radon hazards, and each of these potential sources must be evaluated.

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40. Hazards Associated with Fibrous Minerals

By Malcolm Ross

THE ASBESTOS PROBLEM

The widespread use of amphibole and serpentine asbestos by our industrial society has contributed greatly to human safety and convenience. Yet, while society was accruing these very tangible benefits, many asbestos workers were dying of asbestosis, lung cancer, and mesothelioma. The hazards of certain forms of asbestos under certain conditions have been so great that several countries have taken extraordinary actions to greatly reduce or even ban their use. Recent experiments with animals, however, demonstrate that other fibrous materials can cause the formation of tumors when such particles are implanted within the pleural tissue. These experiments have convinced some health specialists that asbestos-related diseases can be caused by many types of elongate particles; the mineral type, according to these health specialists, is not the important factor in the etiology of disease, but rather the size and shape of the particles that enter the human body.

In the United States, the most widely used definition of asbestos for regulatory purposes comes from the *Federal Register* (October 9, 1975, p. 47652–47660). In this notice, the naturally occurring amphibole minerals amosite, crocidolite, anthophyllite, tremolite, and actinolite and the serpentine mineral chrysotile are classified as asbestos if the individual crystallites or crystal fragments have the following dimensions: a length greater than 5 micrometers, a maximum diameter less than 5 micrometers, and a length-to-diameter ratio of 3 or greater. The crushing and milling of any rock usually produces some mineral particles that are within the size range specified in Federal rules. Thus, these regulations present a formidable problem to those analyzing for asbestos minerals in the multitude of materials and products in which they may be found in some amount.

THE NATURE OF ASBESTOS-RELATED DISEASE

The three principal diseases related to asbestos are (1) lung cancer, (2) mesothelioma (cancer of the pleural and peritoneal membranes), and (3) asbestosis, a condition in which the lung tissue becomes fibrous and thus loses its ability to function. These diseases, however, are not equally prevalent in the various groups of asbestos workers that have been studied; the amount and type of disease depends on the duration of exposure, on the intensity of exposure, and, particularly, on the type or types of asbestos to which the individual has been exposed, generally chrysotile, crocidolite, and (or) amosite (Simpson, 1979; Dupré, 1984).

Chrysotile asbestos (white asbestos) is the form that is usually used in the United States as wall coatings, in brake linings, as pipe insulation, and in other uses. About 95 percent of the asbestos in place in the United States is the chrysotile variety, and a large percentage of this was mined and milled in Quebec Province, Canada. Epidemiological studies of the chrysotile asbestos miners and millers of Quebec show that, for men exposed for more than 20 years to chrysotile dust averaging 20 fibers per cubic centimeter of air, the total mortality was less than expected (620 observed deaths, 659 expected deaths); the risk of lung cancer was slightly increased (48 deaths observed, 42 expected). Exposures to air containing 20 fibers per cubic centimeter are an order of magnitude greater than those experienced now, which are generally less than 2 fibers per cubic centimeter; thus, chrysotile miners working a lifetime under these present dust levels should not be expected to suffer any measurable excess cancer. Mesothelioma incidence among those working only with chrysotile asbestos is very low; thus far, about 16 deaths due to this disease have been reported among chrysotile asbestos miners and millers and one death among chrysotile trades workers (Dupré, 1984, p. 173–178; Ross, 1984, p. 91–93). Four epidemiological studies of the female residents of the Quebec chrysotile mining localities who did not work in the asbestos industry show no statistically significant evidence that their lifelong exposure to asbestos dust from the nearby mines and mills has caused excess disease (Siemiatycki, 1982; Ross, 1984, p. 81–86).

Crocidolite asbestos (blue asbestos) was first imported into the United States in 1912. Epidemiological studies of groups that worked only with crocidolite asbestos show that rather short periods of exposure, or even relatively light exposure, causes excessive mortality due to lung cancer, mesothelioma, and asbestosis. This hazard is evident not only in those exposed to crocidolite during gasmask fabrication and building construction but in those employed in the crocidolite mines. Mesothelioma is a significant cause of death in only two crocidolite mining regions—the Cape Province, South Africa, and Wittenoom, Western Australia. Studies accomplished in the Cape Province show that at least 278 people have died of mesothelioma as a result of exposure to crocidolite; of these people, 161 worked in the mines and mills, and 117 lived in the vicinity of the mines but were not employed in the asbestos industry (Ross, 1984, p. 79–80).

All amosite asbestos (brown asbestos) comes from the Transvaal Province of South Africa, where, between 1917 and 1979, approximately 2.2 million tonnes were mined. Importation of amosite into the United States started in the 1930's. The incidence of asbestos-associated disease in two groups of amosite workers formerly employed at factories in London, England, and Patterson, N.J., was excessive, there being a 18.4 percent lung cancer mortality (117 cases), a 2.8 percent mesothelioma mortality (8 cases), and 4.2 percent asbestosis mortality (27 cases). Only prevalence studies have been made of amosite miners and millers; two individuals have died of mesothelioma. One resident of an amosite mining district has been reported as having died of this disease.

The rock-forming amphibole minerals grunerite and cummingtonite, which are isostructural and chemically similar to amosite (a varietal name for grunerite asbestos), are considered incorrectly by some to be forms of asbestos. Health studies of men mining ores that contain these minerals as gangue do not show any indication of asbestos-related mortality; for example, the Homestake gold miners and the Reserve iron-ore miners (Ross, 1981, 1984).

DISCUSSION

Nonoccupational exposure to chrysotile asbestos, despite its wide dissemination in urban environments throughout the world, has not been shown by epidemiological studies to be a significant health hazard. The same fiber dose-disease response relations observed for chrysotile asbestos do not hold for crocidolite asbestos. Health studies of trades workers exposed to only crocidolite show it to be much more hazardous than chrysotile.

The fear caused by the much exaggerated predictions of the amount of asbestos-related mortality expected in the next 20 or 30 years has generated great political pressure to remove asbestos from our environment and to greatly reduce or even stop its use. An example of this is the concerted effort in several industrial nations, including the United States, to remove asbestos from schools, public buildings, homes, ships, appliances, and so forth. This removal is being done, even though most asbestos is of the chrysotile variety and even though asbestos dust levels in schools, public buildings, and city streets are much lower than those found in chrysotile asbestos mining communities, where no asbestos-related disease has been noted in the nonoccupationally exposed residents. The impetus for these costly removals and appliance recalls (hair dryers, for example) apparently comes from the "zero threshold" concept of cancer induction.

Some health and regulatory specialists classify the common rock-forming amphiboles grunerite, cummingtonite, actinolite, tremolite, and anthophyllite as asbestos even though they do not possess the physical properties requisite to be valuable commercially. Such a classification has been made in the case of taconite mining by the U.S. courts. Thus far, however, asbestos-related disease has not been associated with any mining industry other than commercial asbestos mining.

The possible health effects of exposure to rock dust containing one or more of the many amphibole minerals are an important issue. Amphiboles are contained within the gangue of many hard-rock mines—gold, vermiculite, talc, iron ore, crushed stone and aggregate, copper, and so forth. Certainly, control of most dust, regardless of the mineral content, is necessary because past heavy exposure to dusts containing crystalline silica, slate, coal, talc, and radioactive minerals has caused significant disease. Unusually tight control of amphibole mineral particles, such as was proposed by the National Institute for Occupational Safety and Health in 1976 for asbestos fibers (0.1 fiber per cubic centimeter), however, may stop major mining in the United States.

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41. Environmental Concerns Related to Selenium in the Western United States

By James M. McNeal, Gerald L. Feder, William G. Wilber, *and* Stephen J. Deverel

The form of elements in the natural environment is vitally important in determining their potential for harmful effects to living organisms. Selenium is as an excellent example. Even though the mean concentration of selenium in weathered surficial materials is greater in the Eastern United States than in the Western United States (300 and 230 parts per billion (ppb) selenium, respectively; Shacklette and Boerngen, 1984), selenium toxicity problems are most prevalent in the Western United States, whereas selenium deficiency problems are most prevalent in the Eastern United States. The reason for this reversal is the difference in the chemical form of selenium in the environment and the resultant difference in the ease of aqueous transport of selenium and its availability for plant uptake. This paper discusses the environmental geochemistry of selenium and its relation to environmental effects. This discussion will underscore the importance of the forms of trace elements in understanding, and perhaps predicting and ameliorating, the potentially harmful effects of some elements to the environment.

Environmental problems involving naturally occurring selenium are widespread and have been known for a long time. Rosenfeld and Beath (1964) noted that Marco Polo may have encountered selenium-toxicity problems on his travels to China. They also gave an account of selenium problems in the Western United States and in several other semiarid regions of the world. Even though selenium-toxicity problems are most prevalent in semiarid regions, they may also exist in humid temperate and tropical regions, for example, Ireland and Columbia (Rosenfeld and Beath, 1964).

Selenium is necessary as a trace nutrient to man, but it may also cause toxic effects when ingested in large amounts. In livestock, detrimental effects are known to be caused by selenium in both deficient and excessive amounts. Consequently, much has been written on selenium deficiency and toxicity, particularly in the field of animal nutrition. General texts on selenium include those by Trelease and Beath (1949), Rosenfeld and Beath (1964), and Zingaro and Cooper (1974). Excellent reviews of the natural occurrence of selenium and selenium geochemistry have been written by Lakin (1972, 1973) and Lakin and Davidson (1973). Mineral deposits containing selenium have been discussed by Sindeeva (1964).

The forms of selenium, and other elements, are dependent largely on the pH, the oxidation state, and the chemical constituents of the environment. Geering and others (1968) showed that the weathering of selenium from rocks and its accumulation in soils or ground water depends on the oxidation state and pH of the environment. Some rocks are known to be sources of selenium. For example, some black shales (Lakin, 1973; Leventhal and Hosterman, 1982) and phosphatic deposits (Lakin, 1973) are known to contain high concentrations of selenium.

Selenium predominantly occurs in four forms in the natural environment (Geering and others, 1968). The highly soluble selenate (SeO_4^{2-}) is the form of selenium found in alkaline oxidizing environments. This form of selenium can be readily transported in solution and may be concentrated in closed basins and other areas, particularly in the arid West. As selenate, selenium is readily available for uptake by plants and may concentrate in large amounts in some plants (Rosenfeld and Beath, 1964).

In more acidic environments, selenium tends to occur as selenite (SeO_3^{2-}) ion, which is not as soluble as selenate. Selenite selenium generally occurs as the insoluble basic ferric selenite or may be immobilized by sorption on iron oxyhydroxides. These latter conditions exist largely in the Eastern United States, where the concentration of selenium available to plants may be low. Forage crops grown in these areas sometimes cause selenium deficiency problems in livestock and require the addition of selenium supplements to the soil (Oldfield, 1972).

In more reducing environments, selenium may occur as the metal (Se^0) or the selenide (Se^{2-}) ion. As selenide, selenium may substitute for sulfur in pyrite or other sulfide minerals or may form selenide minerals, for example, tiemannite (HgSe). These forms of selenium are generally immobile in most natural environments, and the rates of transformation between the different forms are slow. Microorganisms are known to reduce selenite to metallic selenium (Ganther, 1974).

The organic chemistry of selenium is similar to that of sulfur. As sulfur is an important constituent of plant and animal tissue (Lakin, 1973), selenium may also be readily incorporated into plant and animal tissue (Ganther, 1974). Some plants, known to accumulate high concentrations of selenium, may be toxic to animals when eaten (Trelease and Beath, 1949; Rosenfeld and Beath, 1964; Ganther, 1974). A relation between the organic content of soils in Ireland and elevated concentrations of selenium was found by Fleming (1962). However, the form of the selenium in the organic material was not determined. Lakin (1972) noted that selenium associated with the organic material of soils occurs as seleniferous proteins, elemental selenium, and selenite. A report on the biochemistry of selenium by Ganther (1974) may be helpful in guiding research on the forms of selenium in the natural environment, which are not well known.

The well-known selenium-toxicity problem at the Kesterson Wildlife Refuge in the west-central part of the San Joaquin Valley in California is due, at least in part, to the mobility of selenium in ground water from adjacent irrigated lands (Deverel and others, 1984). Selenium has been concentrated by evaporation in the areas that have been irrigated over the last 20 to 50 years. Farm drainage systems, which have been installed in some of the irrigated areas in the last 10 to 20 years, are now removing this shallow ground water containing high concentrations of selenium. Current irrigation water provides the hydraulic head necessary to cause the shallow ground water to flow. The accumulation of selenium in Kesterson probably is associated with the discharge of the drainage waters, transmitted by the San Luis Drain, which flow into Kesterson. Analysis of water samples collected at several sites (Deverel and others, 1984) showed selenate to represent over 80 percent of the total dissolved selenium in the sample.

Current environmental concerns with selenium have shown that studies of total element concentrations alone are not satisfactory in evaluating the potential for environmental problems. Most of what is known about selenium in the environment, however, is based on the total concentration of selenium, not on the form of selenium. In addition, the reactions between the various forms of selenium and the constituents of rocks, soils, and sediments (for example, iron oxyhydroxides, manganese oxyhydroxides, organic material, clay minerals, and so on) are not well known. Studies similar to those for selenium should be undertaken for arsenic, molybdenum, uranium and vanadium, among others, because they behave in a geochemical manner similar to that of selenium and may also cause environmental problems.

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42. Copper-Molybdenum Imbalances and the Incidence of Nutritional Diseases in Livestock and Humans

By James A. Erdman

In December 1985, the journal *Minerals and the Environment* changed its name to *Environmental Geochemistry and Health*. In an editorial marking this change, Davies (1985, editorial page) said:

> The composition of food and water are influenced by that of soil which, in turn, depends on the geochemical nature of bedrock. Some rocks naturally contain high concentrations of certain trace elements whereas others are almost devoid of them. These natural geochemical variations are further complicated by localized accumulations of elements, such as cadmium or lead, which arise as a consequence of man's urban, industrial, and mining activities. Some trace elements are essential for mammalian metabolism and deficiencies of them may limit the activities of key enzyme systems or the formation of essential metabolites. Others are toxic.

MOLYBDENOSIS IN ANIMALS

The role of copper and molybdenum in certain nutritional diseases of livestock is well known and widely documented. In animals, molybdenosis results from the interactions of copper, molybdenum, sulfide, and sulfate in the rumen and tissues of cattle, especially, but also of sheep and other ruminants. An excess of molybdenum or sulfate in the diet of ruminants interferes with the absorption of the metabolically required copper in the gastrointestinal tract. Molybdenosis is a worldwide problem occurring not only in the United States but also in Canada, Great Britain, New Zealand, and the Soviet Union.

Venugopal and Luckey (1978, p. 255) gave the following general symptoms of chronic molybdenum intoxication in animals, "loss of body weight, anorexia, anemia, deficient lactation, male sterility owing to testicular degeneration, osteoporosis, and bone-joint abnormalities." Symptoms of acute molybdenum toxicity include severe gastrointestinal irritation and diarrhea, coma, and death from cardiac failure. In sheep, "high levels of soil molybdenum may induce copper deficiency so that newborn lambs are born with defective nervous systems" (Davies, 1985, editorial page). Koval'skii (1977) refers to such a nervous degeneration as endemic ataxia. If treated early enough, molybdenosis is reversible through corrective nutrition.

Historically, molybdenosis was first recognized in the United States in the Central Valley of California and in the sinks of southwestern Nevada where cattle and dairy herds were difficult, if not impossible, to maintain. Research on this problem, therefore, was centered at the University of Nevada, Reno. Newly found regions of molybdenum toxicity now extend from the Pacific Northwest to Colorado and Wyoming (Kubota, 1975).

More recently, work by the U.S. Geological Survey (USGS) documented incidences of this disease as far east as Missouri and farther north into the Dakotas. The Missouri incidence was related to contamination of pastures that were downstream from an abandoned claypit that overflowed in the early 1970's during a prolonged period of heavy rainfall (Case and others, 1973; Ebens and others, 1973). At the time of the incident, USGS personnel had just completed a geochemical survey of the State, and element baselines were available to gauge the severity of the geochemical changes at the claypit. The ranch (Ranch A) immediately adjacent to the claypit received the most severe impact, as was seen in the breeding and calving history of the beef-cattle herds; calf production was halved in the herd affected by the claypit (table 42.1).

Upon completion of the Missouri project, the U.S. Geological Survey began a study of the northern Great Plains lignite province. Some preliminary studies that compared the geochemical environments of reclaimed surface mines in that region revealed a molybdenosis potential at several of the mines (Erdman and others, 1978). As a result of that work, I was contacted by the extension agent in Harding County, S. Dak., about ranchers' reports of problems resembling molybdenosis (poor cow and calf performance and some loss of cattle) in cattle in pastures around an abandoned uraniferous-lignite strip mine at Flint

Table 42.1. Breeding and calving history of three distinct beef-cattle herds on Ranch A for the 1970 and 1971 breeding and calving seasons

[All cows were pasture bred; bulls remained in the pasture from June to September; therefore, most cows calved during March and April of the following year. Numbers in parentheses are percentages. Herd No. 2 ranged on pasture affected by the claypile; herds 1 and 3 were kept on unaffected pastures. The breed of Herds 1 and 2, designated "Angus" in 1970, was changed to "Angus-Charolais" in 1971 because the sires were changed from Angus to Charolais. (From Ebens and others, 1973)]

Herd		Sires		Dams		Cows		Calves			
No.	Breed	Breed	Number (yrs)	Age (yrs)	Breed	Age	Bred	Calved	Born alive	Stillborn	Comments
						1970					
1	Angus	Angus	3	7	Angus	7	54	54 (100)	54 (100)	0 (0)	Brought to ranch in 1966.
2	—do—	—do—	1	2	—do—	4	66	36 (54.5)	31 (86.1)	5 (13.9)	Brought to ranch Oct. 1969 already bred; 7–8 cows rebred.
						1971					
1	Angus-	Charolais	1	9	Angus	8	54	54 (100)	54 (100)	0 (0)	One calf died soon after Charolais birth.
2	—do—	—do—	1	5	—do—	5	66	24 (36.5)	23 (95.8)	1 (4.2)	Undersized dam of stillborn calf died soon after calving.
3	Charolais	—do—	1	4	Charolais	4	24	24 (100)	24 (100)	0 (0)	Two cows had difficulty calving, but recovered. Artificial insemination, in addition to pasture breeding, was used.

Butte. The lignites from the region contain appreciable levels of molybdenum, so much so that the pasturage adjacent to a former ashing plant in North Dakota, where the lignites were burned to concentrate uranium, was found to be toxic to cattle (Christianson and Jacobson, 1971). A study at Flint Butte (Stone and others, 1983), however, showed that the high levels of molybdenum resulted as much from lignites that cropped out in the undisturbed environment as from those lignites exposed during the mining. Stone and others (1983) concluded that, elsewhere in the region, naturally occurring release of molybdenum into the environment from the uranium-bearing lignites may also cause molybdenosis.

Problems with copper-molybdenum imbalances in livestock are far from being resolved in the United States. Copper supplementation in molybdic areas designed to bring copper to optimum levels relative to the molybdenum levels can cause serious side effects (H. Mayland, Agricultural Research Service, Idaho, oral commun., 1986). Salt blocks of copper sulfate have been unsuitable because of the poor control of their use by livestock. Injections of copper glycinate have been used quite widely, but these can cause abscesses that affect the marketability of the livestock. More recently, a copper chelate has been tried, but incidences of cattle deaths following treatment occurred.

Imbalances of copper and molybdenum also exist as a result of other agricultural practices such as liming and clearing woodlands for pastureland. In the Ozarks of southern Missouri, for example, bottomland soils are being overlimed in an attempt to improve yields of alfalfa and clover. According to Dr. Arthur Case, veterinary toxicologist, University of Missouri (written commun., 1986), the molybdenum may be at about normal levels, but the copper is rendered less available because of the increased soil pH. Thus, the copper:molybdenum ratio in the forage is too low for cattle, the critical threshold being 2:1.

MOLYBDENOSIS IN HUMANS

If some animal diseases, such as molybdenosis, can unequivocally be related to the geochemical environment, it is logical to seek evidence for similar links in human health. As Davies (1985) cautioned, establishing a link between environmental geochemistry and human health is not easy, especially in countries like the United States where food production and distribution are so widespread. Incidences of molybdenosis in humans have been reported from less developed countries, however.

Construction of a large dam in southern India has raised the water table in the surrounding district, making the soil more alkaline and thus increasing the molybdenum content in sorghum because molybdenum is more mobile in an alkaline environment. As sorghum is the dietary staple for the local people (Agarwal, 1975), some individuals developed genu valgum (knock-knee), a crippling bone disease affecting young people (fig. 42.1) that probably results from two problems, a molybdenum-induced copper deficiency and fluorosis.

Koval'skii (1977, p. 397–407) described the incidence of endemic gout in Armenia. The inhabitants of the Ankavan molybdenum province depend mostly on local produce, which contains considerably more molybdenum than normal due to soils that are rich in molybdenum but deficient in copper. More molybdenum in the diet increases the synthesis of the metalloenzyme xanthinoxidase and the

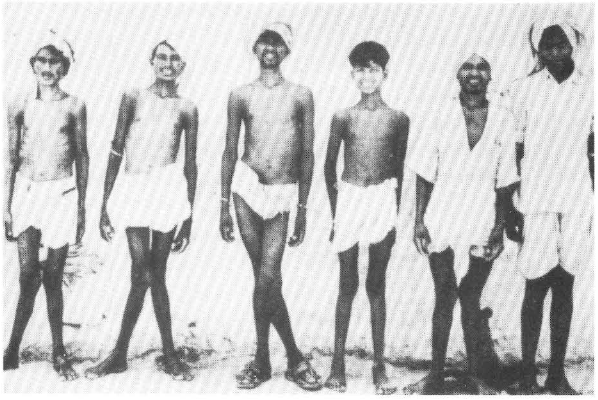

Figure 42.1. Group of young men showing deformity of the knee joint resulting from high dietary intake of molybdenum. This photograph first appeared in *New Scientist*, London (Agarwal, 1975), and is published with their permission.

conversion of xanthine and hypoxanthine into uric acid. "Man, unlike animals, apparently lacks the enzyme urate oxidase that breaks down uric acid. Consequently, uric acid being a relatively insoluble compound, may in some instances be deposited in the tissues of the joints and produce symptoms of gout" (Koval'skii, 1977, p. 190). In a study of 400 individuals from two settlements in the Ankavan province, a direct relation was found between the uric acid content in the blood and length of time spent in the province. The changes seemed to develop quite rapidly, possibly within the first year spent in the area.

Molybdenum-related nutritional problems in humans living in the United States probably do not exist; however, to my knowledge, geochemically oriented epidemiological studies on human health are extremely rare in this country.

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Erdman, J.A., Ebens, R.J., and Case, A.A., 1978, Molybdenosis—A potential problem in ruminants ranging over coalmine spoils: Journal of Range Management, v. 31, p. 34–36.

Koval'skii, V.V., 1977, Geochimicheskaya ekologia [Geochemical ecology]: Ottawa, Department of the Secretary of State, Translation Bureau, Multilingual Services Division, 579 p.

Kubota, J., 1975, Areas of molybdenum toxicity to grazing animals in the Western United States: Journal of Range Management, v. 28, p. 252–256.

Stone, L.R., Erdman, J.A., Feder, G.L., and Holland, H.D., 1983, Molybdenosis in an area underlain by uranium-bearing lignites in the northern Great Plains: Journal of Range Management, v. 36, p. 280–285.

Venugopal, B., and Luckey, T.D., 1978, Metal toxicity in mammals, v. 2 *of* Chemical toxicity of metals and metalloids: New York, Plenum Press, 409 p.

43. Bibliography of Selected Geochemical Studies of the Environment by the U.S. Geological Survey

Compiled by Hansford T. Shacklette, R.C. Severson, *and* Larry P. Gough

[Locations of numbered studies that can be areally plotted are shown on figures 43.1–43.4]

I. GEOCHEMICAL STUDIES OF THE BROADEST SCALE (FIG. 43.1)

Study No. 1a. Soil Geochemistry East and West of the 97th Meridian, Conterminous United States (fig. 43.1).

Boerngen, J.G., and Shacklette, H.T., 1981, Chemical analyses of soils and other surficial materials of the conterminous United States: U.S. Geological Survey Open-File Report 81-197, 145 p.

Shacklette, H.T., 1975, Surficial materials in the conterminous United States (study no. 21), *in* Connor, J.J., and Shacklette, H.T., 1975, Background geochemistry of some rocks, soils, plants, and vegetables in the conterminous United States: U.S. Geological Survey Professional Paper 574–F, p. F9.

Shacklette, H.T., and Boerngen, J.G., 1984, Element concentrations in soils and other surficial materials of the conterminous United States: U.S. Geological Survey Professional Paper 1270, 105 p.

Shacklette, H.T., Boerngen, J.G., Cahill, J.P., and Rahill, R.L., 1973, Lithium in surficial materials of the conterminous United States and partial data on cadmium: U.S. Geological Survey Circular 673, 8 p.

Shacklette, H.T., Boerngen, J.G., and Keith, J.R., 1974, Selenium, fluorine, and arsenic in surficial materials of the conterminous United States: U.S. Geological Survey Circular 692, 14 p.

Shacklette, H.T., Boerngen, J.G., and Turner, R.L., 1971, Mercury in the environment—Surficial materials of the conterminous United States: U.S. Geological Survey Circular 644, 5 p.

Shacklette, H.T., Hamilton, J.C., Boerngen, J.G., and Bowles, J.M., 1971, Elemental composition of surficial materials in the conterminous United States: U.S. Geological Survey Professional Paper 574–D, 71 p.

Study No. 1b. Chemical Data for Elements in Water at Selected Locations.

Anderson, B.M., 1971, Calcium-carbonate hardness in public water supplies in the conterminous United States, *in* Environmental geochemistry of health and disease: Geological Society of America Memoir 123, p. 151–153.

———1972, Lithium in surface and ground waters of the conterminous United States: U.S. Geological Survey Open-File Report 72–0006, 7 p.

Fleischer, Michael, 1962, Fluoride content of ground water in the conterminous United States (maximum reported value for each county): U.S. Geological Survey Miscellaneous Geologic Investigations Map I–387, scale 1:5,000,000.

Study No. 1c. Geochemical Studies of the Western Energy Region, Northern Great Plains, and Parts of the Rocky Mountains (fig. 43.1).

Askenasy, P.E., and Severson, 1988, Chemical procedures applicable to overburden and mine soil, chap. 4, *in* Hossner, L.R., ed., Reclamation of surface-mined lands, v. 1: Boca Raton, Fla., CRC Press, p. 55–80.

Connor, J.J., 1975, Surface soils and sagebrush, Wyoming and Montana (study no. 35), *in* Connor, J.J., and Shacklette, H.T., Background geochemistry of some rocks, soils, plants, and vegetables in the conterminous United States: U.S. Geological Survey Professional Paper 574–F, p. F100.

———1982, The need for experimental design in trace element geochemistry [abs.], *in* Gough, L.P., and Severson, R.C., eds., Trace-element mobilization in western energy regions—Proceedings of a symposium held November 21–24, 1982, in Denver, Colorado: Golden, Colo., Colorado School of Mines Research Institute Press, p. 2.

Crock, J.G., and Severson, R.C., 1980, Four reference soil and rock samples for measuring element availability in the western energy regions: U.S. Geological Survey Circular 841, 16 p.

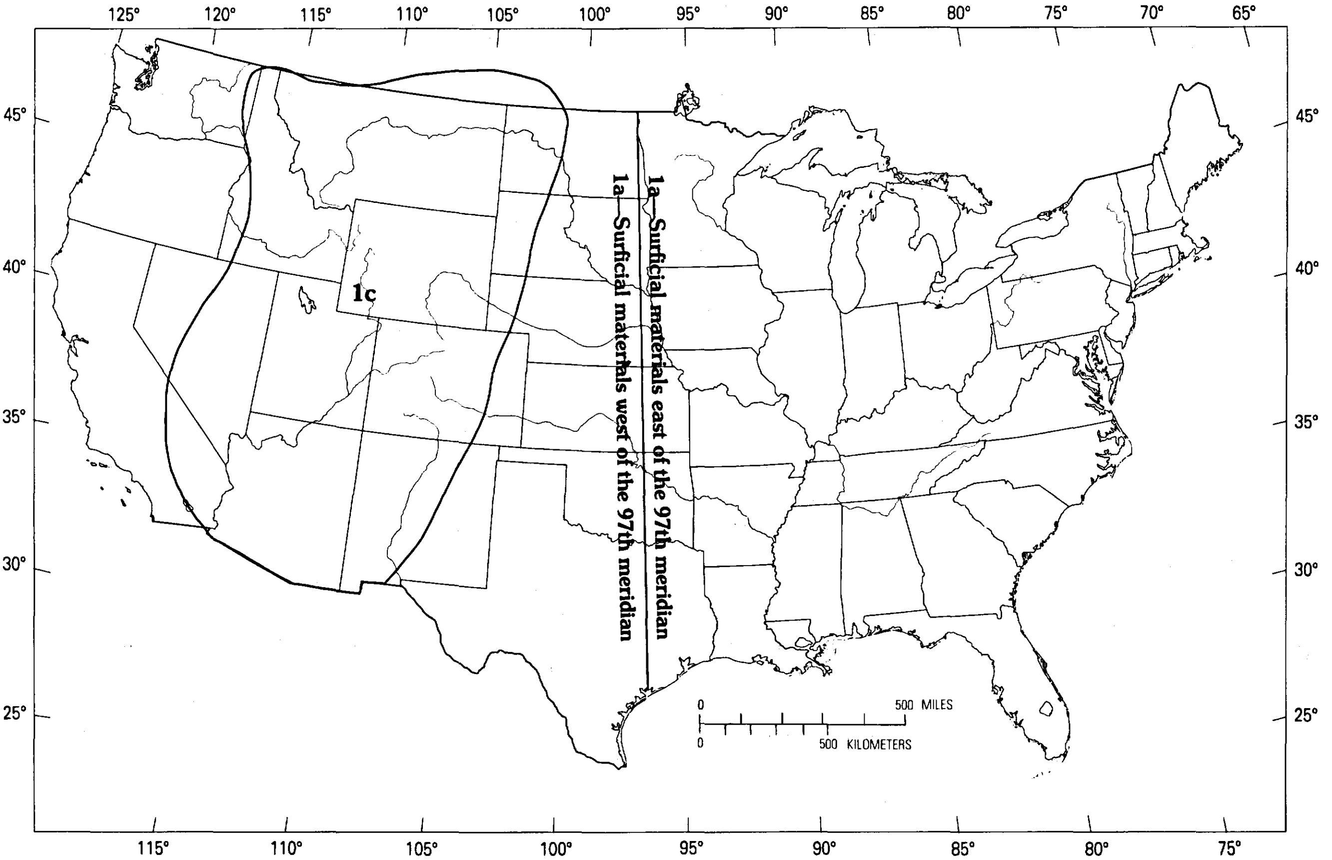

Figure 43.1. Geochemical studies of the broadest scale in the conterminous United States. 1a, Soil geochemistry east and west of the 97th meridian; 1c, Geochemical studies of the western energy region, northern Great Plains, and parts of the Rocky Mountains.

Ebens, R.J., and McNeal, J.M., 1982, Shale and sandstone of the Fort Union Formation in the northern Great Plains (study no. 1), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237 p. 4.

Erdman, J.A., and Gough, L.P., 1982, Miscellaneous small grains from the northern Great Plains (study no. 21), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 19.

Feder, G.L., 1982, Ground water chemistry, Poplar River basin, Montana and Saskatchewan (study no. 27), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 24.

Gough, L.P., McNeal, J.M., and Severson, R.C., 1980, Predicting native plant copper, iron, manganese, and zinc levels using DTPA and EDTA soil extractants, northern Great Plains: Soil Science Society of America Journal, v. 44, no. 5, p. 1030–1036.

Gough, L.P., and Severson, R.C., 1981, Trace metal toxicity assessment at 11 Western United States surface coal mines [abs.]: Madison, Wisc., American Society of Agronomy, Agronomy Abstracts, p. 26.

———1982, Trace element mobilization in western energy regions—Proceedings of a symposium held November 21–24, 1982, in Denver, Colorado: Golden, Colo., Colorado School of Mines Research Institute Press, 50 p.

———1983, Rehabilitation materials from surface coal mines in Western U.S.A., pt. II, Biogeochemistry of wheatgrass, alfalfa, and fourwing saltbush: Reclamation and Revegetation Research, v. 2, p. 103–122.

Gough, L.P., Severson, R.C., and McNeal, J.M., 1982, Soils and native plants, northern Great Plains (study no. 18), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 16-17.

Herring, J.R., Hinkley, T.K., and Ebens, R.J., 1982, Geochemistry of sandstones from the Fort Union Formation, northern Great Plains (study no. 4), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 6.

Hinkley, T.K., and Ebens, R.J., 1982, Geochemistry of fine-grained rocks in cores of the Fort Union Formation (study no. 3), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 6.

Jackson, L.L., Engleman, E.E., and Severson, R.C., 1985, Characterization of the forms of sulfur in overburden materials of the Western United States, *in* Proceedings, 2d annual meeting of the American Society of Surface Mining and Reclamation, Denver, Colo., October 8–10, 1985: Princeton, W. Va., American Society for Surface Mining and Reclamation, p. 49a–49d.

McNeal, J.M., 1982, Stream-sediment chemistry in the northern Great Plains (study no. 6), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 9.

———1985, The occurrence of extractable elements in soils from the northern Great Plains: Soil Science Society of America Journal, v. 49, p. 873–881.

McNeal, J.M., Lee, D.E., and Millard, H.T., Jr., 1981, The distribution of uranium and thorium in granitic rocks of the Basin and Range province, Western United States: Journal of Geochemical Exploration, v. 14, no. 1, p. 25–40.

Miesch, A.T., 1975, Sandstone, shale, and carbonate rocks of the Sauk sequence of Precambrian, Cambrian, and Ordovician age on the cratonic part of the Western United States (study no. 3), *in* Connor, J.J., and Shacklette, H.T., Background geochemistry of some rocks, soils, plants, and vegetables in the conterminous United States: U.S. Geological Survey Professional Paper 574–F, p. F3–F6.

Severson, R.C., and Fisher, S.E., Jr., 1985a, Results of the 1st Western Task Force Round Robin Soil and Overburden Analysis Program: U.S. Geological Survey Open-File Report 85–220, 58 p.

———1985b, Western soil and overburden task force group round robin analyses in 1984–1985, *in* Proceedings, 2d annual meeting of the American Society for Surface Mining and Reclamation, Denver, Colo., October 8–10, 1985: Princeton, W. Va., American Society for Surface Mining and Reclamation, p. 90a–90c.

———1986, Results of the 2d Western Task Force Round Robin Soil and Overburden Analysis Program: U.S. Geological Survey Open-File Report 86–49, 30 p.

Severson, R.C., and Gough, L.P., 1983a, Rehabilitation materials from surface coal mines in Western U.S.A., pt. I, Chemical characteristics of spoil and replaced cover-soil: Reclamation and Revegetation Research, v. 2, p. 83–102.

———1983b, Boron in mine soils and rehabilitation plant species at selected surface coal mines in Western United States: Journal of Environmental Quality, v. 12, p. 142–146.

———1984, Rehabilitation materials from surface-coal mines in Western U.S.A., pt. III, Relations between elements in mine soil and uptake by plants: Reclamation and Revegetation Research, v. 3, p. 185–197.

Severson, R.C., Gough, L.P., and McNeal, J.M., 1977, Availability of elements in soils to native plants, northern Great Plains: U.S. Geological Survey Open-File Report 77–847, 93 p.

Severson, R.C., and Tidball, R.R., 1979, Spatial variation in total element concentration in soil within the northern Great Plains coal region: U.S. Geological Survey Professional Paper 1134–A, 18 p.

———1982, Total soil chemistry, northern Great Plains (study no. 16), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p.16.

Shultz, L.G., Tourtelot, H.A., Gill, J.R., and Boerngen, J.G., 1980, Composition and properties of the Pierre Shale and equivalent rocks, northern Great Plains region: U.S. Geological Survey Professional Paper 1064–B, 114 p.

Tidball, R.R., 1978, Chemical and mineralogical evaluation of soils, Hanging Woman Creek EMRIA site, Big Horn County, Montana: U.S. Geological Survey Open-File Report 78–346, 88 p.

Vine, J.D., and Tourtelot, E.B., 1973, Geochemistry of lower Eocene sandstones in the Rocky Mountain region: U.S. Geological Survey Professional Paper 789, 36 p.

Area No. 2. Soil and Plant Geochemistry, Alaska (fig. 43.2).

Gough, L.P., Peard, J.L., Severson, R.C., Shacklette, H.T., Tompkins, M.L., Stewart, K.C., and Briggs, P.H., 1984, Chemical analyses of soils and other surficial materials, Alaska: U.S. Geological Survey Open-File Report 84–423, 79 p.

Gough, L.P., and Severson, R.C., 1981, Element concentrations in rehabilitation species from thirteen coal-strip mines in the five Western States and Alaska: U.S. Geological Survey Open-File Report 81–182, 118 p.

Gough, L.P., Severson, R.C., and Shacklette, H.T., 1988, Element concentration in soils and other surficial materials in Alaska: U.S. Geological Survey Professional Paper 1458, 53 p.

Severson, R.C., and Gough, L.P., 1983, Chemical composition and variability of soils from the Capps coal field, Alaska: U.S. Geological Survey Open-File Report 83–190, 36 p.

———1984, Estimated physiological tolerance ranges for selected elements in soils, Capps coal field, *in* Reed, K.M., and Bartsch-Winkler, Susan, eds., The United States Geological Survey in Alaska; accomplishments during 1982: U.S. Geological Survey Circular 939, p. 75–78.

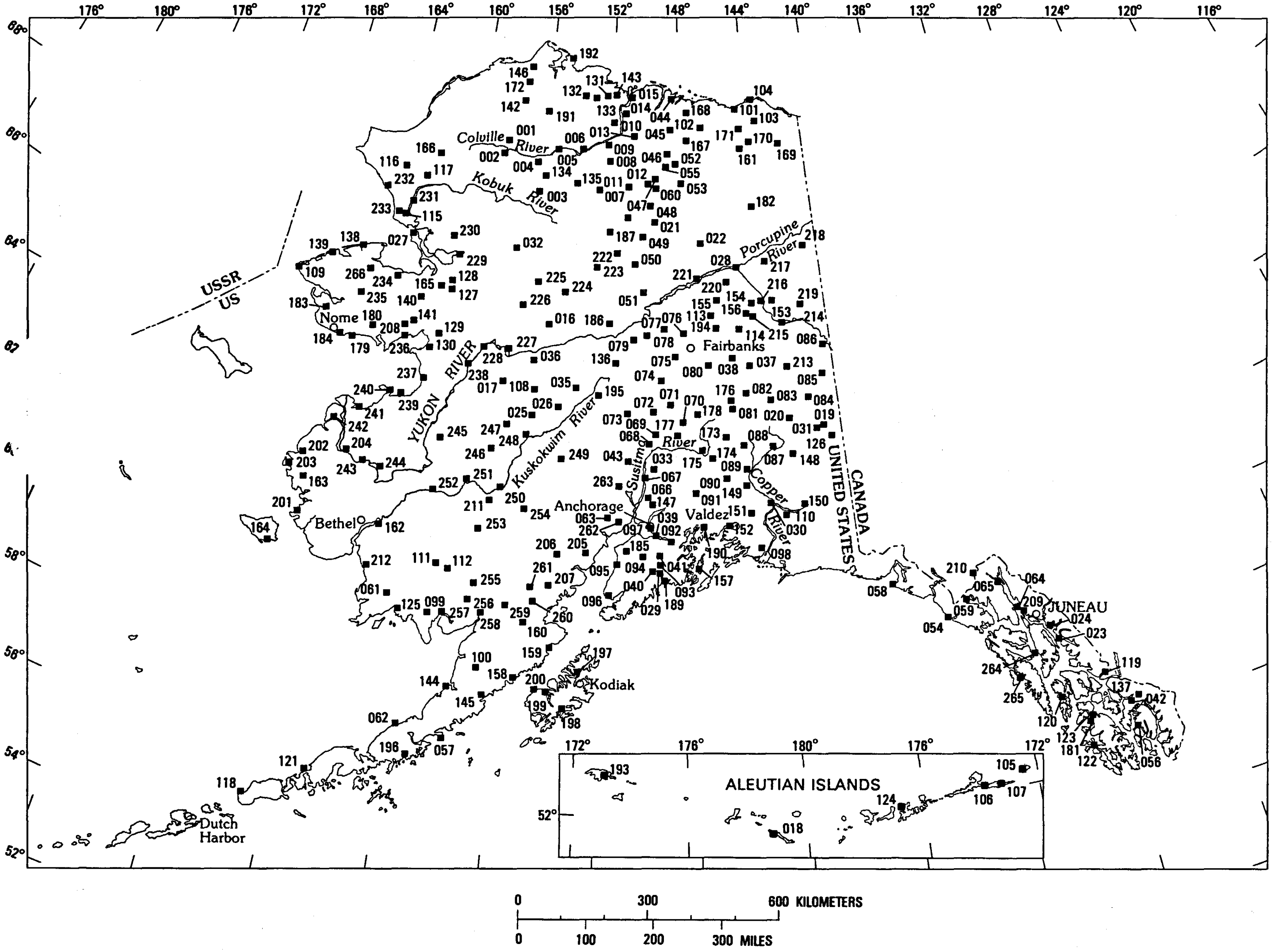

Figure 43.2. Geochemical studies of the broadest scale in Alaska. Map shows studies of soil and plant geochemistry in Alaska. Numbers refer to studies listed in Gough and others (1988).

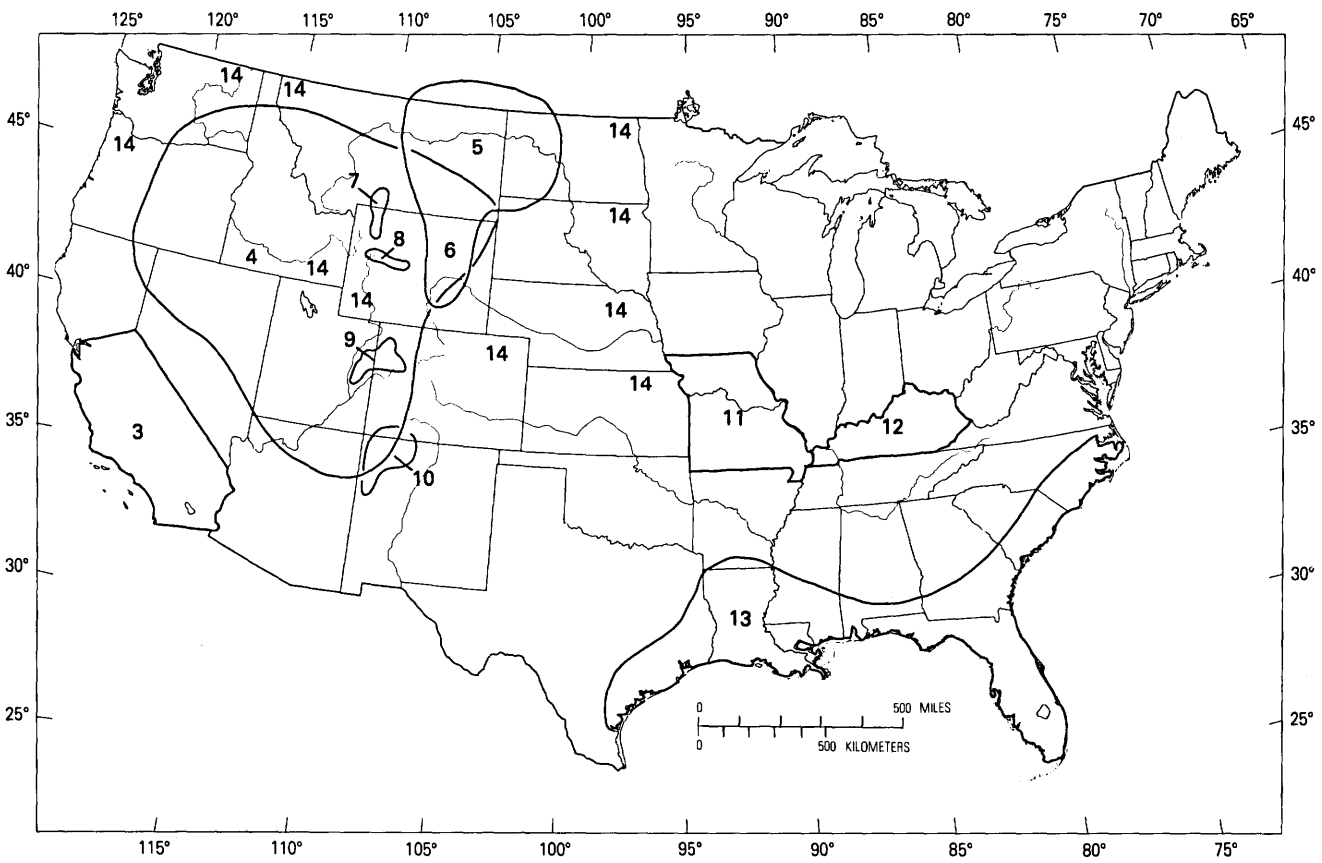

Figure 43.3. Locations of numbered regional geochemical studies (3–14) of rocks, stream sediments, soils, plants, and waters.

II. REGIONAL GEOCHEMICAL STUDIES OF ROCKS, STREAM SEDIMENTS, SOILS, PLANTS, AND WATERS (FIG. 43.3).

Study No. 3. California Stream Sediments.

McNeal, J.M., 1985, Regional-scale geochemical mapping in the United States, *in* Thornton, Iain, ed., Proceedings of the 1st International Symposium on Geochemistry and Health, April 16–17, 1985, London, England: London, Science Reviews, Ltd., Monograph Series, Environmental Geochemistry and Health, p. 16-30.

McNeal, J.M., and Miller, W.R., 1982, Regional geochemical mapping of the Southern Coast Ranges, California, using stream sediments and heavy-mineral concentrates [abs.], *in* Program with Abstracts, Ninth International Geochemical Exploration Symposium, Saskatoon, Saskatchewan, Canada: Ontario, Canada, Association of Exploration Geochemists, p. 116–117.

McNeal, J.M., Miller, W.R., and Motooka, J.M., 1982, Geochemical mapping of the distribution of elements in stream sediments, Southern Coast Ranges, California [abs.]: Geological Society of America, Abstracts with Programs, v. 14, no. 4, p. 214.

Study No. 4. Elements in Big Sagebrush.

Connor, J.J., Keith, J.R., and Anderson, B.M., 1982, Trace-metal variation in soils and sagebrush in the Powder River Basin, Wyoming and Montana (study no. 20), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 17–19.

Erdman, J.A., and Harrach, G.H., 1981, Uranium in big sagebrush from Western U.S. and evidence of possible mineralization in the Owyhee Mountains of Idaho: Journal of Geochemical Exploration, v. 14, no. 1, p. 83–94.

Gough, L.P., and Erdman, J.A., 1982, Big sagebrush from eight western physiographic provinces (study no. 23), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 21.

———1983, Baseline elemental concentrations for big sagebrush from Western U.S.A.: Journal of Range Management, v. 36, no 6, p. 718–722.

Area No. 5. Fort Union Region.

Ebens, R.J., and McNeal, J.M., 1982, Shale and sandstone of the Fort Union Formation in the northern Great Plains (study no. 1), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 4.

Feder, G.L., 1982, Ground-water chemistry, Fort Union coal region (study no. 25), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 21.

Herring, J.R., Hinkley, T.K., and Ebens, R.J., 1982, Geochemistry of sandstones from the Fort Union Formation, Northern Great Plains (study no. 4), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 6.

Hinkley, T.K., and Ebens, R.J., 1982a, Geochemistry of fine-grained rocks in cores of the Fort Union Formation (study no. 3), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 6.

———1982b, Chemical and mineralogical analyses of core samples from Hanging Woman Creek, Montana (study no. 2), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 6.

Tidball, R.R., 1982, Chemical and mineralogical evaluation of soils, Hanging Woman Creek, Montana (study no. 14) *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 13–14.

Area No. 6. Powder River Region.

Anderson, B.M., Keith, J.R., and Connor, J.J., 1975, Antimony, arsenic, germanium, lithium, mercury, selenium, tin, and zinc in soils of the Powder River Basin, *in* Geochemical survey of the western coal regions, 2d annual progress report, July 1975: U.S. Geological Survey Open-File Report 75–436, p. 50–57.

Connor, J.J., Denson, N.M., and Hamilton, J.C., 1976, Geochemical discrimination of sandstones of the basal Wasatch Formation, Powder River Basin, Wyoming and Montana, *in* Laudon, R.B., ed., Geology and energy resources of the Powder River; Wyoming Geological Association, 28th annual field conference guidebook: Casper, Wyoming Geological Association, p. 291–297.

Connor, J.J., Keith, J.R., and Anderson, B.M., 1976, Trace-metal variation in soils and sagebrush in the Powder River Basin, Wyoming and Montana: U.S. Geological Survey Journal of Research, v. 4, no. 1, p. 49–59.

———1982, Trace-metal variation in soils and sagebrush in the Powder River Basin, Wyoming and Montana (study no. 20), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 17–19.

Erdman, J.A., and Gough, L.P., 1982, Soil lichens from the Powder River Basin (study no. 22), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 19–21.

Feder, G.L., 1982, Ground-water chemistry, Powder River coal region, Montana and Wyoming (study no. 28), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 24.

Keith, J.R., Anderson, B.M., and Connor, J.J., 1974, Trace-metal variation in the Powder River Basin, *in* Geochemical survey of the western coal region, 1st annual progress report, July 1974: U.S. Geological Survey Open-File Report 74–250, p. 14–29.

McNeal, J.M., Keith, J.R., Anderson, B.M., and Boerngen, J.G., 1982, Chemistry of Powder River sediments (study no. 7), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 9.

Tidball, R.R., 1975, Sampling requirements for mapping soil geochemistry in the Powder River Basin, Montana-Wyoming, *in* Geochemical survey of the western coal region, 2d annual progress report, July 1975: U.S. Geological Survey Open-File Report 75–436, p. 20–28.

Tidball, R.R., and Ebens, R.J., 1976, Regional geochemical baselines in soils of the Powder River Basin, Montana-Wyoming, *in* Laudon, R.B., ed., Geology and energy resources of the Powder River; Wyoming Geological Association, 28th annual field conference guidebook: Casper, Wyoming Geological Association, p. 299–310.

———1982, Soils of the Powder River Basin, Wyoming and Montana (study no. 13), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 13.

Tidball, R.R., Erdman, J.A., and Ebens, R.J., 1975, Geochemical baselines for sagebrush and soil, Powder River Basin, Montana-Wyoming, *in* U.S. Geological Survey, Geochemical survey of the western coal regions, 1st annual progress report, July 1974: U.S. Geological Survey Open-File Report 74–250, p. 6–13.

Area No. 7. Bighorn River Region.

Severson, R.C., 1979, Regional soil chemistry in the Bighorn and Wind River Basins, Wyoming and Montana: U.S. Geological Survey Professional Paper 1134–B, 9 p.

———1982, Soil geochemistry of the Wind River and Big Horn Basins, Wyoming and Montana (study no. 17), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 16.

Area No. 8. Wind River Region.

Severson, R.C., 1979, Regional soil chemistry in the Bighorn and Wind River Basins, Wyoming and Montana: U.S. Geological Survey Professional Paper 1134–B, 9 p.

———1982, Soil geochemistry of the Wind River and Big Horn Basins, Wyoming and Montana (study no. 17), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 16.

Area No. 9. Uinta-Piceance Region.

Anderson, B.M., 1982a, Effects of processed oil shale on the element content of *Atriplex canescens*: U.S. Geological Survey Open-File Report 82–1051, 18 p.

———1982b, Trace element content of *Atriplex canescens* from the Colorado State University oil shale revegetation plot, Piceance Basin, Colorado [abs.], *in* Gough, L.P., and Severson, eds., Trace element mobilization in western energy regions—Proceedings of a symposium held November 21–24, 1982, Denver, Colorado: Golden, Colo., Colorado School of Mines Research Institute Press, p. 40.

Dean, W.E., 1982, Geochemistry of an oil shale core, Piceance Creek Basin, Colorado (study no. 5), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 6–9.

Dean, W.E., Ringrose, C.D., and Klusman, R.W., 1982, Soils of the Piceance Creek Basin, western Colorado (study no. 15), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 14–16.

McNeal, J.M., and Feder, G.L., 1982, Stream-sediment chemistry of the Uinta and Piceance Creek Basins, Utah and Colorado (study no. 8), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 11.

McNeal, J.M., Ringrose, C.D., and Klusman, R.W., 1982, Geochemical variability of sediments from two streams in the Piceance Creek Basin, Colorado (study no. 9), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 11.

Tidball, R.R., and Severson, R.C., 1977, Chemical variation in alluvial soils in the oil shale region, *in* Geochemical survey of the western energy regions, fourth annual progress report, July 1977: U.S. Geological Survey Open-File Report 77–872, p. 55–64.

———1982, Alluvial soils of the Piceance Creek and Uinta Basins (study no. 12), *in* Ebens, R.J., and Shacklette, H.T., Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, p. 13.

Tuttle, M.L., Ackerman, D.J., Dean, W.E., Briggs, P.H., and Bartel, A.N., 1983, Chemical and mineral composition data on oil shale and reported oil-shale wastes from Rulison, Colorado: U.S. Geological Survey Open-File Report 83–378, 32 p.

Tuttle, M.L., Dean, W.E., and Ackerman, D.J., 1985, An evaluation of the effects of weathering on a 50-year old reported oil-shale waste pile, Rulison experimental report, Colorado, *in* Gary, J.H., ed., Eighteenth Oil Shale Symposium Proceedings: Golden, Colo., Colorado School of Mines Press, p. 338–346.

Tuttle, M.L., Severson, R.C., Dean, W.E., and Klusman, R.W., 1986, Geochemical variability of soils and biogeochemical variability of plants in the Piceance Basin, Colorado, *in* Geochemical survey of the western energy regions: U.S. Geological Survey Professional Paper 1134–E, 46 p.

Area No. 10. San Juan Basin Region—Rock, Soil, and Plant Chemistry.

Gough, L.P., and Severson, R.C., 1981, Biogeochemical variability of plants at native and altered sites, San Juan Basin, New Mexico, *in* Geochemical survey of the western energy regions: U.S. Geological Survey Professional Paper 1134–D, 26 p.

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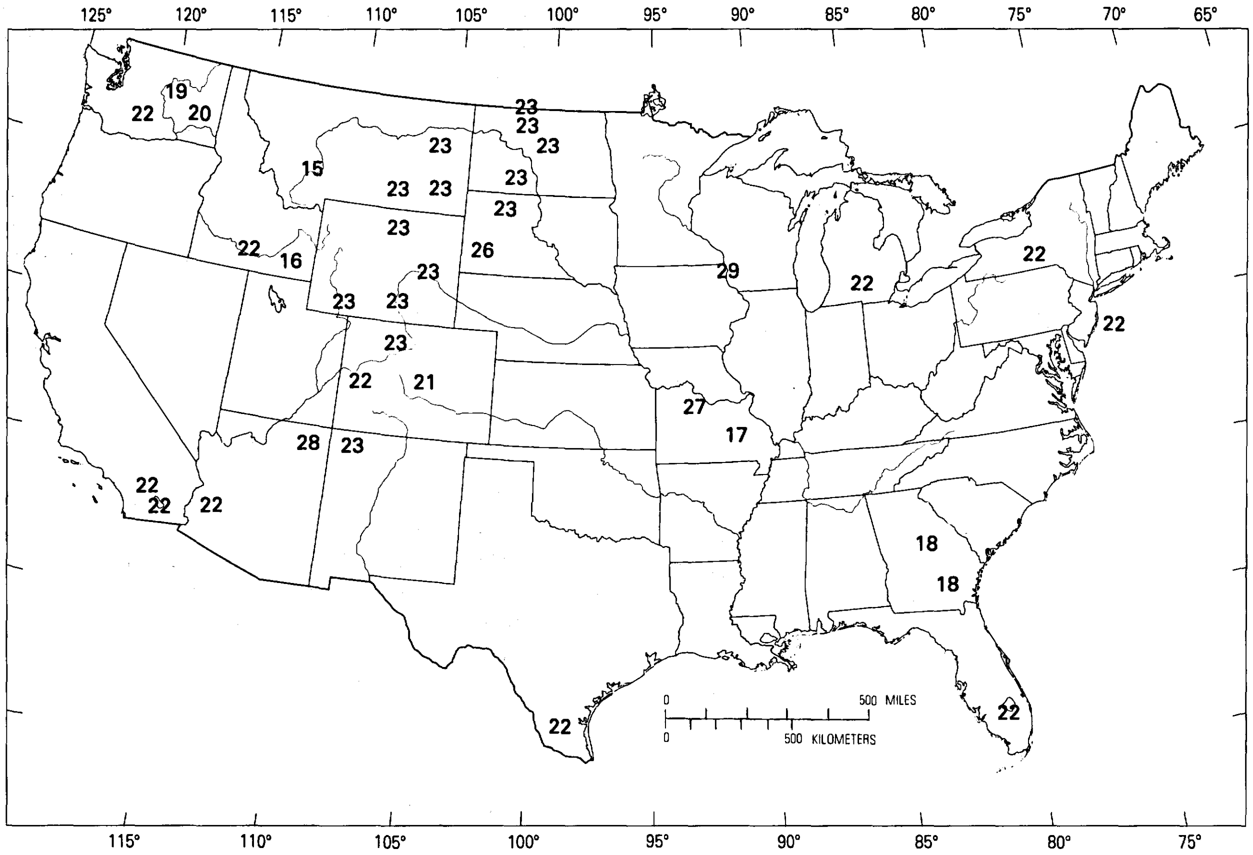

Figure 43.4. Locations of numbered geochemical studies (15–23, 26–29) of rocks, soils, and plants—the effects of pollution and relation to human and animal nutrition and disease.

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