Joint U.S. Geological Survey, U.S. Nuclear Regulatory Commission Workshop on Research Related to Low-Level Radioactive Waste Disposal, May 4-6, 1993, National Center, Reston, Virginia, Proceedings

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CONVERSION FACTORS, VERTICAL DATUM, ABBREVIATED WATER-QUALITY UNITS, AND MULTIPLICATION FACTORS

Multiply	By	To obtain
pascal (Pa)	1 X 10^{-5}	bar
becquerel (Bq)	0.027027	curie
centimeter per year (cm/yr)	0.3937	inch per year
cubic meter (m^3)	35.31	cubic foot
gram (g)	0.03527	ounce
hectare (ha)	2.471	acre
kilograms per day (kg/d)	2.2046	pounds per day
kilometer (km)	0.6214	mile
liter (L)	33.82	ounce, fluid
megagram (Mg)	1.102	short ton
meter (m)	3.281	foot
meter per year (m/yr)	3.281	foot per year
metric ton (t)	1.102	short ton
millimeter (mm)	0.03937	inch
square centimeter (cm^2)	0.1150	square inch
square kilometer (km^2)	0.3861	square mile
square meter (m^2)	10.7643	square foot

Factor by which unit is multiplied	Prefix	Symbol
10^{3}	kilo	k
10^{2}	hecto	h
10	deka	da
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	µ
10^{-9}	nano	n
10^{-12}	pico	p

Chemical concentrations and water temperature are given in metric units. Chemical concentration is given in milligrams per liter (mg/L). Radon activity is given in picocuries per liter (pCi/L). Water temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation:

$$°F = 1.8(°C) + 32$$

Sea Level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

JOINT U.S. GEOLOGICAL SURVEY, U.S. NUCLEAR REGULATORY COMMISSION WORKSHOP ON RESEARCH RELATED TO LOW-LEVEL RADIOACTIVE WASTE DISPOSAL PROCEEDINGS

Edited by Peter R. Stevens *and* Thomas J. Nicholson

INTRODUCTION

This report contains papers presented at the "Joint U.S. Geological Survey (USGS) and U.S. Nuclear Regulatory Commission (NRC) Technical Workshop on Research Related to Low-Level Radioactive Waste (LLW) Disposal" that was held at the USGS National Center Auditorium, Reston, Virginia, May 4-6, 1993. The objective of the workshop was to provide a forum for exchange of information, ideas, and technology in the geosciences dealing with LLW disposal. This workshop was the first joint activity under the Memorandum of Understanding between the USGS and NRC's Office of Nuclear Regulatory Research signed in April 1992.

Participants included invited speakers from the USGS, NRC technical contractors (U.S. Department of Energy (DOE) National Laboratories and universities) and NRC staff for presentation of research study results related to LLW disposal. Also in attendance were scientists from the DOE, DOE National Laboratories, the U.S. Environmental Protection Agency, State developmental and regulatory agencies involved in LLW disposal facility siting and licensing, Atomic Energy Canada Limited (AECL), private industry, Agricultural Research Service, universities, USGS and NRC.

The workshop topics, selected jointly by USGS and NRC staff, focused on technical subjects in the geosciences related to LLW disposal. Five topical areas were selected to organize the sessions. A brief description of the five topics follows:

1. Surface- and Ground-Water Pathway Analysis—The specific subtopics discussed were interrelationship of climatic variability, microbiological processes, the aqueous transport of colloids, and ground-water modeling for performance assessment. Eight papers relating to this topic provide insight into the significance and complexity of the hydrologic and biologic processes, the degree of understanding of the processes, and the uncertainty in estimating the relevant parameters. A discussion of the role of ground-water models in performance assessments provides a perspective on the state-of-the-art in practice.
2. Ground-Water Chemistry—Certain environmental tracers useful for age-dating of ground-water and evaluating hydrogeologic processes were discussed. Other topics presented were: some geochemical processes affecting contaminant transport; the results of modeling chemical processes in particular aquifer systems; and the implications regarding modeling solute transport. Six papers were presented.

Two papers discuss the use of environmental tracers and light stable isotopes in age-dating of young ground waters and in identifying flow paths. Two papers describe the partitioning and distribution of various radionuclides between solution, particulates, colloids, and organic complexes in surface and ground waters. Also, two papers discuss modeling of geochemical reactions with emphasis on understanding water-rock-gas interactions and the complementarity of geochemical and hydrological modeling.

3. Infiltration and Drainage—This session focused on current practices concerning measurement and prediction of infiltration and drainage, and identification of relevant processes and their uncertainties and information needs for their resolution. The following questions were raised:
    - What are the gaps in the understanding of relevant processes and unresolved technical issues?
    - How sound are current models of isothermal flow of water in homogeneous, non-swelling media?
    - How well are the multi-phase flow aspects of infiltration and drainage understood and how are they to be treated?
    - How complete is our knowledge of parametric functions appearing in theories of infiltration and drainage?
    - How do we deal with the complexity represented by ordinary field settings?
    - What assumptions are required to model infiltration and drainage?
    - What field studies are needed to evaluate models of infiltration and drainage and assess their degree of uncertainty?

    The first paper provides an overview regarding the application of unsaturated flow theory to infiltration and drainage and reiterates the questions posed above. The following nine papers provide insight to these questions and discuss the following topics: Laboratory measurement of unsaturated hydraulic conductivities at low water contents; Use of environmental tracers to identify preferential flow through fractured media and to quantify drainage; Field experiments to evaluate relevant processes affecting infiltration and drainage; and The use of deterministic and stochastic models for simulating flow and transport through heterogeneous media.
4. Vapor-Phase transport and volatile radionuclides—The following questions were raised:
    - What processes affect vapor-phase transport through heterogeneous porous and fractured media?
    - How well are non-isothermal vapor flow processes understood?
    - How much is known about barometrically driven vapor flow?
    - How well are the multi-phase flow aspects of infiltration and drainage understood (those aspects related to convective flow of unsaturated-zone gases and to the trapping of non-wetting-phase fluids)?
    - What assumptions are required to model vapor-phase movement?
    - What field studies are needed to evaluate vapor-phase transport models and to assess their degree of uncertainty?

    The first paper on this topic focuses on numerical simulation of coupled air-water systems and presents a global pressure/fractional flow formulation of the governing equations as an approach to develop efficient numerical algorithms. The second paper discusses the escape of the volatile radionuclides, tritium and ^{14}C, from the low-level waste disposal site in a humid environment, the flux of carbon dioxide through the trench caps, and the accumulation of ^{14}C by plants on the trench caps. The third paper discusses the rate and maximum depth of water percolation in a very arid site and summarizes data suggesting that below shallow depths the flux of water in both the liquid and vapor phase is upward.

5. Ground-water flow and transport field studies—The following questions were raised:
   - What significant lessons have been learned concerning dispersion and scale effects for various hydrogeologic settings from field studies?
   - To what extent can transport modeling needs, especially uncertainty assessments, be incorporated into experimental field design?
   - What field studies are needed to help resolve uncertainties in fluid flow and transport modeling?

The papers on this topic discuss improvements in our understanding of processes and new techniques of assessing ground-water flow and transport in both porous and fractured crystalline rocks resulting from field studies. These studies have employed innovative techniques and multidisciplinary approaches to field problems that are very complex and difficult and costly to conduct. Many of these field studies are continuing studies, and although the results cannot be anticipated at this time, hold the promise of additional contributions to our understanding of flow and transport processes and innovative techniques that will facilitate evaluation of prospective disposal sites.

At the conclusion of the workshop, the session chairs and recorders prepared summaries of these five topical sessions. These summaries follow this introduction and precede the presented papers.

The workshop proceedings are published here as a USGS Water-Resources Investigations Report. The approaches and/or methods described in the proceedings are provided for information only. They are not intended as a substitute for NRC regulations, and compliance with suggestions or recommendations contained in this report is not required. Publication of this report does not necessarily constitute NRC approval or agreement with the information contained herein.

Topic I—Surface- and Ground-Water Pathway Analysis

By Thomas E. Reilly *and*
Andrew Campbell

Summary of Presentations

This session addressed a range of topics including paleohydrology, surface and ground-water transport, microbiological processes and solute transport modeling. No common technical issues permeated the session. However, most of the speakers did indicate that analysis of surface- and ground-water pathways required insight into the various hydrologic processes, and that the processes have an inherent uncertainty, both in the estimation of relevant parameters, and in the understanding of the processes themselves.

Three papers focused on surface-water processes. Robert Jarrett described the use of paleohydrology in analyzing floods and droughts. These studies provide a means of assessing the magnitude and frequency of major flooding events over long time frames (for example, 10,000 yr), whereas instrumental records (about 20 yr) and historical records (100-200 yr) may not capture the full variability. This information is particularly important in establishing design basis events for a particular site and assessing the risks to engineered structures.

Releases from uranium mining and milling operations in the Grants Mineral Belt of New Mexico, which led to increased levels of radioactivity in the Puerco River, were discussed by John Gray and Peter Van Metre. Much of the increase was associated with suspended sediments. Uranium mill tailings represent a voluminous form of low-level radioactive waste generally disposed of in surficial impoundments. Edward Landa addressed the geochemical forms of radionuclides in these tailings, potential mobilization mechanisms, the extent of sorption, and microbiological effects. Due to its high radioactivity, ^{226}Ra is generally the uranium daughter product of most concern.

Hydrologic processes occurring in both surface water and shallow ground water were addressed by three papers. Boby Abu-Eid and his colleagues discussed three major issues in decommissioning contaminated sites: (1) developing and applying appropriate retardation values (K_d) for a site; (2) determining the solubility of uranium in specific site soils; and (3) approaches for selecting appropriate ground-water transport models and code limitations. Two significant problems in selecting K_d values are: (a) poor reproducibility of established laboratory methods; and (b) use of average K_d values based upon widely varying experimental conditions for a specific site. Another important problem is matching site characterization with contamination transport model requirements.

Derek Lovley presented studies of the effects that an isolated bacterial strain can have on the mobility of uranium (U) in natural soil systems, and possible development of bio-remediation techniques using microbial reduction of U (VI) to U(IV). Laboratory studies demonstrate that enzymatic reduction by live microbes plays an important role in determining the mobility of uranium in natural soils and sediments.

Richard Harnish and his associates discussed particulate, colloidal, and solution phase associations of plutonium, americium, and uranium in surface and ground water at the Rocky Flats Plant, Colorado. This talk focused on field and laboratory work to determine the size fractions of the radionuclides in ground water and surface waters near the plant. Plutonium was primarily in the particulate fraction, whereas uranium was entirely in the dissolved fraction. Although americium was mainly found in the particulate fraction, it showed some variability in the colloidal fraction, which may be important for its transport.

Two papers dealt with the use of numerical models in regulatory decision making. Natalie Olague and associates presented different models to simulate the same experiment, not to find the 'best' fit but to provide guidance to the regulatory community. They suggested that model discrimination tests, such as those presented, be used on site-specific experiments.

Clifford Voss focused on the use of numerical models as tools that are a part of an analysis of a hydrologic system for regulatory assessment. Because numerical models are only tools, the important transferable knowledge gained by the skillful analyst is in the report that describes the knowns, unknowns, and insights gained through the analysis process. The author stated that because there is significant uncertainty in describing and understanding hydrogeologic systems, ground-water models are only valuable for intuition building (increasing our level of understanding), not for quantitative prediction of consequences.

Topic II—Ground-Water Chemistry

By Donald T. Thorstenson *and*
D. Kirk Nordstrom

Summary of Presentations

The papers in Session II can be conveniently grouped as follows: two papers (Schilk and Robertson; Kraemer) described the partitioning and distribution of various radionuclides between solution, particulates, colloids, and organic complexes in surface and ground waters; two papers (Plummer and Busenberg; Coplen), dealt with the use of tracers and light stable isotopes in identifying flowpaths and dating of young (less than 50 yr old) ground waters; and two papers (Parkhurst; Nordstrom) dealt with modeling of chemical reactions and transport. The topics discussed also seemed to fall naturally into two categories--those dealing with sites in which contamination is already present in natural systems, and studies whose principal application would appear to lie in the characterization of potential future sites. In Session II (as in Session I) most discussion centered on the modeling studies.

Schilk and Robertson, Kraemer (and Harnish and others, Session I), illustrate the utility of field-scale characterization of the partitioning of radionuclides among phases. The approaches used in these studies are a necessary first step in understanding processes necessary for remediation of already-contaminated sites and to provide guidelines to avoid similar problems in future sites. Radionuclides do not partition similarly between aqueous, particulate, colloidal, and organically-complex forms even in the same environments at Rocky Flats, and the widely varying and extreme chemical environments that can occur at the single site (Chalk River) complicate matters further. Kraemer's Mississippi River studies, in particular, illustrate the difficulty of identifying, even on a continental scale, a non-anthropogenic level of radionuclides. These studies serve to illustrate the great complexity of attempts to understand processes in presently contaminated environments, and the tremendous gulf that remains to be bridged before even rudimentary reaction transport modeling of such systems can be attempted.

The applicability of deuterium and ^{18}O isotopes to low-level waste studies can be summarized concisely. If source waters of different isotopic signatures can be identified in a given system, these isotopes can provide extremely valuable and quantitative information for tracing these waters in a given hydrologic system. Coplen also showed that on a short time scale, and for the very local geographic scale, seasonal variability in deuterium and ^{18}O can provide flow-velocity information. To the degree that these conditions are met, these techniques should be applicable to both present and future disposal sites.

Data for chlorofluorocarbons (CFC's), tritium/^{3}He, and ^{85}Kr can give concordant ages in shallow ground-water systems. The CFC's in particular appear to have the potential for providing exceptionally detailed flow information at potential disposal sites, and for interpreting the modification of such flow regimes during post-emplacement. Because of the large number of potential anthropogenic sources, the CFC's will probably be of little or no utility within contaminant plumes. Tritium/^{3}He, however, has a potential for use within a plume if no extraneous ^{3}He sources are present—a possible dating/tracer technique that should be evaluated. The CFC's also provide a powerful technique for studying transport processes in unsaturated zones. Sampling/analytical difficulties will perhaps preclude the common use of ^{85}Kr.

The inverse chemical modeling studies consisted of two small-scale inverse geochemical modeling efforts at Stripa, Sweden, and the Poços de Caldas, Brazil, natural analog site. In each case, sets of chemical reactions that are consistent with spatial distribution of water chemistry and mineralogy were identified. These are not transport or flow models; in fact they assume a knowledge of flow paths (but not rates) for their application. On a regional scale, working with major reactions identified by inverse modeling, Parkhurst applied a one-dimensional reaction transport model (a forward modeling problem) to the Central Oklahoma aquifer system. The model successfully simulates sequences of reactions and minerals, and provides estimates of rates of migration of various reaction fronts through the system. Perhaps one of the most important features was the model analysis that showed that the two parameters to which the model is most sensitive were P(CO_2) in the unsaturated zone and the total amount of exchangeable sodium in the system.

The Session II presentations and discussions can perhaps be summarized as follows. The most important aspects of completed investigations at presently contaminated sites will lie in providing guidelines for design, construction, and siting of future waste separation, packaging, and disposal procedures. The tracers and dating tools, in combination with chemical and hydrologic modeling—site specific—can provide pre-emplacement characterization and thus a reference for perturbations during the post emplacement period. Perhaps with adequate preliminary information, the most important contribution of modeling will be in conjunction with post-emplacement monitoring programs.

Topic III—Infiltration and Drainage

By David E. Prudic *and* Glendon Gee

Summary of Presentations

Infiltration into and drainage from facilities for the disposal of low-level radioactive wastes is considered the major process by which non-volatile contaminants are transported away from the facilities. The session included 10 papers related to the processes of infiltration and drainage, and to the simulation of flow and transport through the unsaturated zone. The first paper, presented by David Stonestrom, was an overview regarding the application of unsaturated flow theory to infiltration and drainage. Stonestrom posed three basic questions, which are:

1. How well do we know the relevant processes affecting flow and transport?
2. How well can we measure the parametric functions used to quantify flow and transport?
3. How do we treat complexities inherent in field settings?

The other nine papers presented during the session gave some insight to these questions. Topics included: laboratory measurement of unsaturated hydraulic conductivities at low water contents, by John Nimmo; use of environmental tracers to identify preferential flow through fractured media and to quantify drainage, by Edmund Prych and Edwin Weeks; field experiments to evaluate relevant processes affecting infiltration and drainage, by Brian Andraski, Glendon Gee, and Peter Wierenga; and the use of deterministic and stochastic models for simulating flow and transport through heterogeneous sediments, by Richard Hills, Lynn Gelhar, and Shlomo Neuman.

The papers describing field experiments concentrated on arid regions reflecting the recent interest in siting disposal facilities in thick unsaturated zones. The processes affecting flow and transport through the unsaturated zone in arid regions are not well understood. Although the papers emphasized infiltration and drainage through sediments in arid regions, the general concepts are also applicable to humid regions because the processes affecting flow and transport are the same.

Accurate measurements of hydraulic properties are important in quantifying infiltration and drainage. Saturated hydraulic conductivities of sediments can be obtained using a variety of field and laboratory methods. Unsaturated hydraulic conductivities are more difficult because they are non-linear functions of water content and pressure head. Unsaturated hydraulic conductivities are usually estimated from water-retention data. Rarely, however, do these analyses provide reliable estimates of unsaturated hydraulic conductivity at the low moisture contents measured in the field. The steady-state centrifuge method described by Nimmo can accurately determine unsaturated hydraulic conductivity at low-water contents for several types of uniform sediments. Improvements to the method are being considered to test a wider variety of sediments encountered in nature.

Recharge to ground water can be continuous and spatially distributed as a result of widespread percolation or it can be transient and concentrated as a result of percolation of water through distinct pathways. Weeks presented evidence of preferential flow at two sites; one at the Idaho National Engineering Laboratory, and the other at the Nevada Test Site. The evidence is based on differences in concentrations of chlorofluorocarbons and dissolved constituents of samples collected in the unsaturated zone to concentrations determined from the underlying ground water. He concluded that the various methods for estimating diffuse recharge do not apply at the two sites; rather recharge is focused along pathways that bypass the greater part of the unsaturated-zone volume.

Both chloride mass balance and ^{36}Cl techniques can be used to estimate long-term rates of deep percolation. Prych applied both methods to estimate diffuse percolation through sediments at the Hanford facilities in eastern Washington. The use of ^{36}Cl as an indication of transport through the unsaturated zone is extremely valuable because fallout of ^{36}Cl from bomb testing during the 1950's resulted in a peak concentration that can be traced in the sediments.

Results of field experiments at the Hanford facilities and near Beatty, Nevada, by Gee and Andraski respectively, indicate that deep percolation of precipitation through trench covers is likely unless deep-rooted vegetation is allowed to grow on the usually denuded covers. Furthermore, Gee noted that although model simulations are useful in exploring the scope of a problem, simulations did not adequately predict actual flow over extended times even though the model had been calibrated to observed data. He attributed this inability to accurately predict flow to uncertainties in parameters used in the model. Andraski noted that the practice of not vegetating the covers over the buried wastes at the disposal facilities near Beatty increased the potential for deep percolation and suggested that such practices be re-evaluated in the siting of future facilities.

Field experiments, such as the one constructed at Las Cruces, New Mexico, and described by Wierenga, are important to furthering the understanding of infiltration and drainage at disposal facilities, and in providing a means for testing deterministic and stochastic models of flow and transport. Wierenga's data on drainage through layered sediments allowed detailed testing of both types of models, as described by Hills. Such tests illustrate the importance of collaboration between experimenters and modelers in jointly designing field experiments. Data collected during the experiment suggests that even in sediments that seem fairly uniform, variability of hydraulic properties can be large even over distances of less than a meter. Simulations using both deterministic and stochastic models of varying complexities consistently overestimate the first arrival times of a wetting front and underestimate the vertical location of the centroid of the drainage plume at later times. The results also showed that more complex models do not necessarily lead to better predictions.

The applicability of stochastic modeling of flow and transport was discussed by Gelhar and Neuman. They argued that stochastic models are always needed because of the heterogeneity and uncertainty inherent in flow and transport through layered geologic deposits. Gelhar outlined several outstanding needs, including: development of better direct methods for determining unsaturated hydraulic-conductivity functions; development of practical stochastic site-characterization methods; and development of simplified models that incorporate the uncertainty in the distribution of hydraulic parameters. In addition to incorporating the heterogeneity of the sediments, Neuman described the importance of scale on the treatment of model parameters. He noted that no matter what the scale of measurement, there is always a good chance of missing processes that occur at a smaller scale. Neuman closed the discussion of stochastic modeling by summarizing:

> We have to use a stochastic framework when dealing with uncertainty in all cases. It does not matter if the problem concerns low-level or high-level radioactive waste sites. It does not matter if the flow is saturated or unsaturated. I am quite convinced that deterministic models which do not originate from a stochastic framework are a figment of our imagination when we lack a deterministic description of the system being modeled. Deterministic models can and should be derived formally from a stochastic framework; such models describe the behavior of conditional means, or predictors, of unknown quantities such as heads, concentrations, and fluxes. The stochastic framework relates deterministic model parameters to the scale, quantity, and quality of the available data. It further allows assessing the uncertainity associated with such "deterministic" predictions.

On the basis of the papers presented during the session and the ensuing discussion, progress is being made in understanding processes affecting infiltration and drainage through unsaturated heterogeneous sediments. Such progress is important in determining the relative merits and adequacy of sites for disposal of low-level radioactive wastes. Field experiments, similar to those described in the session, combined with improved methods of directly determining unsaturated hydraulic-conductivity functions, and improved methods of incorporating heterogeneity and scale into models, are needed to improve accuracy in predicting contaminant migration from waste-disposal facilities.

Topic IV—Vapor-Phase Transport and Volatile Radionuclides

By Michael Celia *and* Donald C. Thorstenson

Summary of Presentations

This session focused on different aspects of contaminant transport in the vapor phase. The presentations demonstrated the important couplings between water and air flow in the unsaturated zone, for movement of both water and contaminants. The presentations also demonstrated the potential importance of air-phase transport as an exposure pathway at low-level waste sites.

The first presentation of the session focused on numerical simulation of coupled air-water systems. Using simulations, the appropriateness of Richards' equation was shown. The dynamic response of the air phase, independent of whether or not Richards' equation is valid for water movement, was also shown. Numerical methods were discussed briefly, and a global pressure/fractional flow formulation of the governing equations was presented as an approach to develop highly efficient numerical algorithms. Transport equations were presented for both air and water, with phase-change terms including both equilibrium and kinetic expressions. Time scales and the resolution of short-time events, specifically at the land surface boundary, were discussed.

Two ongoing studies are being carried out at sites near West Valley, New York, and at a second site near Beatty, Nevada. The hydrology at these two sites is totally different, and as a result, so are the major technical issues addressed at each site.

The West Valley site is in the humid northeast. At this site, shallow burial in a fine-grained till produced variable accumulation of water in the site trenches. Much of the waste is thus under water and subject to biological degradation under oxic or anoxic redox conditions that vary with location at the site, and seasonally in individual trenches. The degradation processes are similar to those in many landfills, and are responsible for one of the principal concerns at this site, namely the escape of the volatile radionuclides tritium and ^{14}C. This problem has been recognized since the early 1970's. The principal volatile compounds are tritiated water vapor and methane, and $^{14}CO_2$ and methane. Two additional aspects of this problem—the flux of carbon dioxide through the trench caps, and the accumulation of ^{14}C by plants on the trench caps are addressed in the paper by McConnaughey. The plant uptake studies in particular have produced surprising results regarding the mechanism of bioaccumulation.

The second site is near Beatty, Nevada, in a highly arid environment with annual precipitation averaging less than 100 mm/yr. Trenches at this site are far above the water table and are thus continuously dry. Rates of biodegradation of organic waste are unknown, but presumed to be slow. Also, unknown, but anticipated to be much less a problem than at West Valley, are the volatile fluxes of ^{14}C and tritium. The major issue at the Beatty site is the rate of water percolation in this arid environment. The available data suggest infiltration rates on the order of 1 mm/yr, with no net recharge to depths greater than 10 m. The available preliminary data suggest that the flux of both liquid and vapor water is upward. The paper by Prudic discusses the data leading to these conclusions, and illustrates the difficulty of determining a parameter as fundamental as the direction of water flow in arid environments.

Topic V— Ground-Water Flow and Transport Field Studies

By Christopher Neuzil *and* Clifford Voss

Summary of Presentations

Session V of the workshop had as its theme field studies of ground-water flow and transport. In many respects these are the most difficult, yet most significant phase, in the investigation of subsurface flow and transport, particularly in efforts related to waste confinement. Ultimately, it will be our understanding of various sites, through field studies, that will allow us to make informed decisions regarding the siting of repositories and the risks that such facilities present. This may, in turn, influence engineering decisions about constructed barriers.

Despite the fundamental importance of field study, this aspect of ground-water hydrology arguably has lagged significantly behind conceptual and analytical development. There are many reasons for this. Perhaps most significant are the difficulty and cost of field investigation, as well illustrated by several of the participants in Session V. In the first paper, Dennis LeBlanc attempted to give a sense of what it was like to conduct the tracer tests carried out by him and his colleagues at a research site on Cape Cod. These tests, recognized as perhaps the most definitive of their type, involved a large planning effort and an even greater effort to conduct. In order to characterize the fine detail of tracer plumes hundreds of multi-level sampling wells had to be installed along the plume path, and tens of thousands of water samples collected as the plume passed. Moreover, efficient techniques of sampling waters and keeping track of the samples had to be devised and implemented. These studies were successful due to the relative homogeneity of the sediments at the site.

Another example of the effort required to conduct a definitive field study was provided by Paul Hsieh and Allen Shapiro in their presentations on the Mirror Lake research site. This study of a fractured crystalline rock site is utilizing the talents of a wide variety of researchers to attack this difficult problem from a multidisciplinary base. For example, hydraulic testing, in itself a difficult, costly, and time consuming task, is being supplemented by geochemical studies of stable and radioactive natural tracers, geological studies of the lithologies and fracturing, and both surface and downhole geophysical characterization of the heterogeneity (as described by Pete Haeni). Clearly, field studies with this degree of integration are tremendously complex, and correspondingly difficult and costly to conduct. The element of risk represented by field studies is well illustrated here as well; despite the state-of-the-art effort being applied at this site, it is unclear how definitive the resulting characterization of the flow and transport system will be.

As a third illustration of the difficulty of field investigations we can cite the planned investigation of glacial till in New York described by Richard Yager in his presentation. This study is designed to investigate not only the properties of the till as it is in its natural state, but also to characterize its behavior in a repository environment and to evaluate the properties of various types of grouts which might be used. This will require installation of a caisson in the till which is large enough for workers to enter in order to perform experiments and take samples. The proposed effort is similar to work that has already been done in Nevada and described in an earlier session by Dave Prudic. It is obvious that such investigations are difficult and costly.

Along similar lines was the work done by Robert Schultz and described by Edward O'Donnell on characterizing the effectiveness and longevity of engineered covers for waste disposal facilities. This required constructing actual covers at a similar scale to real facilities. These experiments showed that the ability of various covers to exclude recharge varies greatly. One result that would have been difficult to anticipate was the effectiveness of drought-resistant cedars for intercepting infiltration in a cover. As part of this presentation David Smiles described a proposed experiment to examine the diffusive transport of tritium on field scales in the unsaturated zone.

A circumstance that distinguishes ground-water studies is our inability to control our "experiments;" the domains with which we work are complex, irregular, and heterogeneous. Because we cannot prespecify the conditions in domains of interest we must instead carefully characterize them. Indeed, such characterization is the reason we must go to the lengths that we do in field studies. Even the most extensive field studies, however may not provide the information required, particularly if only well established techniques are employed. Innovative approaches are continually being developed and employed to this end. A good example of this was provided by Pete Haeni in his description of new geophysical techniques which have been used at the Mirror Lake study site. Directional borehole radar is just now beginning to be used to locate fractures and determine their attitude, and has shown promise as a mapping tool at Mirror Lake at distances of 30 to 40 m from the borehole. Another relatively new technique, tomography, has also been tried with some success.

Innovative approaches may also entail the employment of established concepts in unconventional ways. This was well illustrated by Warren Wood in his talk on the significance of diffusion. Usually relegated to a secondary role in field-scale transport problems, diffusion apparently can be quite important in some situations. Wood showed, for example, that sand grains from the Cape Cod site mentioned earlier have an internal connected porosity of 10 percent. Solutes can therefore diffuse into the grains. Wood attributed some of the lag and spreading in the lithium plume at Cape Cod to sorption within the sand grains themselves. Diffusion can also apparently play an important role in determining the water quality in fractured crystalline rocks, allowing release of solutes from intact blocks of rock to fractures.

In the realm of waste disposal, ground-water scientists are being asked to consider time-scales considerably longer than those typically of concern in engineering. One way to examine processes which operate over long time scales is to analyze analogous situations in the geologic past which may have evolved over long periods of time. One such study was described by Grant Garven and Jeff Raffensperger, wherein they considered the Cigar Lake uranium deposits in Canada which were formed by the transport of uranium-rich fluids in a thick sand deposit. Simulations of multispecies reactive solute transport in variable density flow with heat transport suggest that free convection in the permeable sands due to heat flow from below were sufficient to account for the formation of these deposits. Garven reminded attendees that the local scale flow systems considered by many of the speakers are often components of much larger systems, requiring that the large-scale perspective be considered before evaluating smaller scales.

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REPORTS

PALEOHYDROLOGY AND ITS VALUE IN ANALYZING FLOODS AND DROUGHTS

By Robert D. Jarrett

Introduction

The environmental and economic importance of major floods and droughts emphasizes the need for a better understanding of hydrometeorologic processes and of related climatic and hydrologic fluctuations or variability. In the United States, the average annual flood damage for the 10-yr period 1979-88 was $2.4 billion and the average annual number of deaths for the period 1925-88 was 95. Droughts lack the dramatic physical results of floods because droughts develop gradually with time and throughout a geographic area, and they affect people and the economy (water supply, ground-water levels, water quality, agriculture, navigation, hydroelectric power, fisheries, and recreation) in different ways. Therefore, identifying the effects and estimating the loss of life and damage from a drought are difficult.

Estimating the magnitude and frequency of large floods and droughts and their effect on people also is difficult. One of the primary missions of the U.S. Geological Survey is to operate a streamflow-gaging-station network to monitor the Nation's water resources and to evaluate streamflow extremes. Estimates of the frequency of floods, droughts, and long-term streamflow variability from short-term (generally much less than 100 yr) data records contain much uncertainty. Paleohydrologic techniques offer a way to lengthen a short-term data record and, therefore, to reduce the uncertainty in hydrologic analysis. Paleohydrology, as discussed here, is the study of the evidence of the movement of water and sediment in stream channels before the time of continuous (systematic) hydrologic records or direct measurements. Paleohydrologic data typically have been used to quantitatively reconstruct hydrologic variability for about the last 10,000 yr. Paleohydrology complements existing data, extends our hydrologic knowledge, and allows the reconstruction of long-term hydrologic records. Paleohydrologic studies have been done throughout the United States and in many other countries.

Techniques

Paleohydrologic analysis uses many types of proxy data. Evidence of historic and prehistoric floods commonly is preserved in stream channels as distinctive sedimentologic deposits or landforms and also can be preserved as botanical evidence. The interpretation of this evidence provides important supplemental information about the spatial occurrence, magnitude, age, and frequency of floods, droughts, and hydrologic variability. Most paleohydrologic techniques used for reconstructing discharge are either for floods or for variations of long-term discharge by using a variety of geomorphic, botanic, and hydraulic approaches. Many different paleohydrologic techniques are used to date material present on the land surface.

Application

Until recently, most planning related to water resources rarely has been able to consider long-term hydrologic variability or climatic change; thus, water-resources investigations and planning sometimes are hampered by inadequate and (or) erroneous hydrologic data. Short records that include large floods or extreme droughts also might cause significant uncertainty in the results of frequency analysis. Because of the small sample of large floods and extreme droughts in the short systematic streamflow record, conventional hydrologic analysis might not always provide the most accurate representation of the frequency of floods and droughts or long-term hydrologic variability. The use of paleohydrologic techniques provides one means of evaluating the hydrologic effects of long-term hydrologic variability and climatic change because it complements existing short-term systematic and historical records, provides information at ungaged locations, and helps decrease the uncertainty in hydrologic estimation.

Commonly, risk from floods and droughts must be evaluated for time scales beyond the length of available systematic records. Examples include flood-plain management, hydrologic aspects of dam safety, and siting of nuclear power plants and waste-storage facilities. Climatic influences on floods, droughts, and long-term hydrologic variability are discussed in this section.

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Uranium-mining Releases From the Grants Mineral Belt to the Little Colorado River Basin, Arizona and New Mexico

By John R. Gray *and* Peter C. Van Metre

Introduction

The USGS studied the presence of radionuclides and other trace metals downgradient from uranium-mining activities in New Mexico's Grants Mineral Belt during 1988-91. This paper summarizes the occurrence and probable sources of selected radionuclides in streamflow and near-channel alluvial ground water of the Puerco River, Arizona and New Mexico.

Background

Releases from uranium mining and milling operations in the Grants Mineral Belt of New Mexico resulted in increased levels of radioactivity in the Puerco River and parts of its near-channel aquifer, within the Little Colorado River Basin of Arizona and New Mexico (fig. 1). Major uranium deposits in the Westwater Canyon Member of the Morrison Formation of Jurassic age of the Grants Mineral Belt of New Mexico were mined from shafts averaging 500 m deep that extended below the water table. Water seeping into as many as three mine shafts was pumped in 1960-61 and 1967-86 to prevent shaft flooding. Effluent was released to Pipeline Arroyo, a small tributary of the naturally ephemeral Puerco River. In the absence of runoff, the effluent evaporated or infiltrated the stream channel.

Before the mid-1970's, untreated mine effluent was released directly into Pipeline Arroyo. Beginning in the mid-1970's, effluent was treated in ponds using barium chloride to coprecipitate radium and a flocculent to reduce suspended solids concentrations. A separate ion exchange treatment reduced average dissolved-uranium concentrations by about 85 percent from 1975-82.

On July 16, 1979, a tailings pond dike failed at the United Nuclear Corporation uranium mill near Pipeline Arroyo. The resulting spill was the largest single release of uranium tailings liquid in U.S. history. An estimated 360,000 m^3 of uranium mine tailings liquid and 1,000 Mg of tailings were discharged to the Puerco River via Pipeline Arroyo. The pH of the tailings liquid was about 1.6, and the total gross-alpha activity

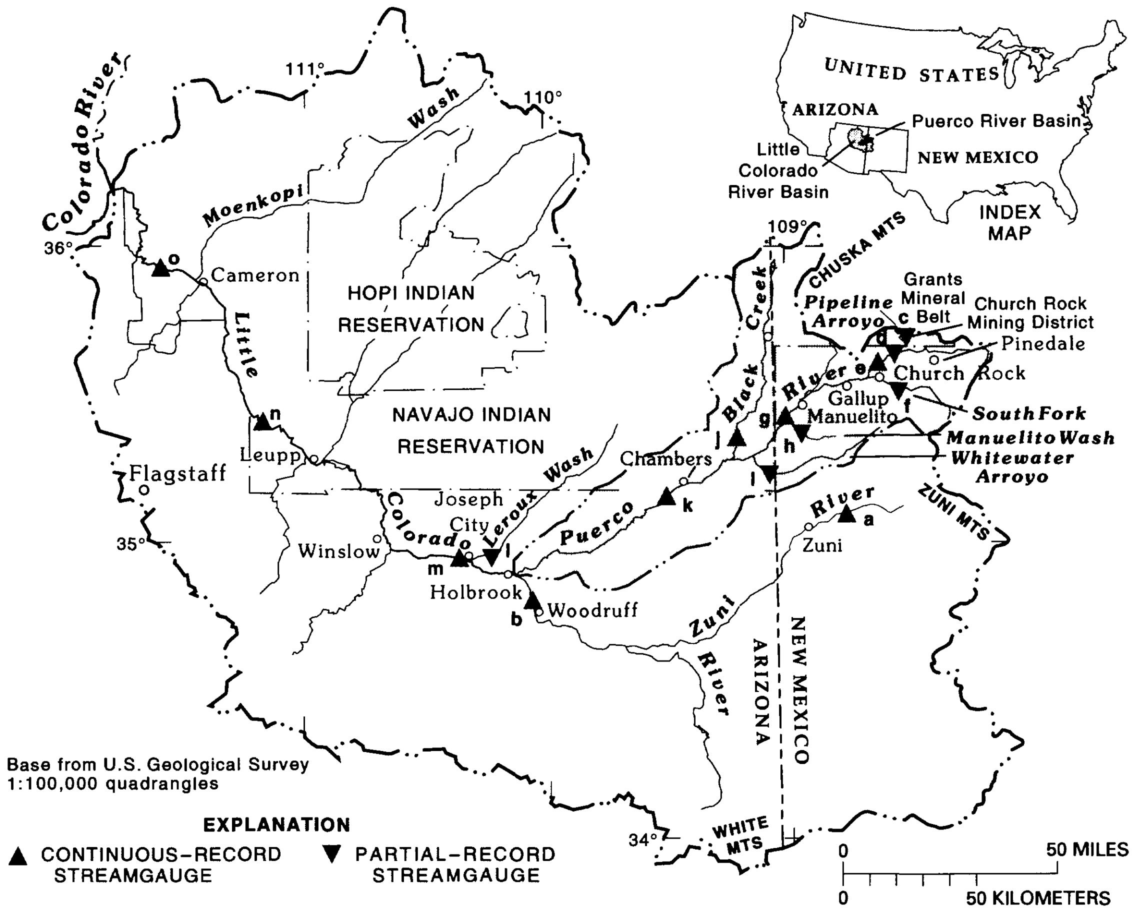

Figure 1. Location of Little Colorado River and Puerco River basins and stream gages. Section of figure 2 runs from k to f along the Puerco River.

was estimated as 130,000 pCi/L. Table 1 lists selected water-chemistry constituents measured in the tailings solution and spill water (P.C. Van Metre, L. Wirt, T.J. Lopes and S.A. Ferguson, U.S. Geological Survey, written commun., 1993.

A reconnaissance-level study by the USGS on the water chemistry of the Puerco River alluvial aquifer in 1986 indicated that water from 5 of 14 shallow wells contained gross-alpha (minus uranium and radon) activities equal to or larger than the U.S. Environmental Protection Agency's (EPA) maximum contaminant level (MCL) for drinking water of 15 pCi/L (Webb and others, 1987). Puerco River streamflow samples collected in Arizona from 1979-85 typically contained total gross-alpha plus gross-beta activities of several thousand pCi/L, or ranging from about 1 to 3 orders of a magnitude larger than Arizona's maximum allowable limit of 30 pCi/L of gross-alpha plus gross-beta activity in surface water (Gray and Webb, 1991; Wirt and others, 1991).

Concern expressed by officials and residents near the Puerco River over the effects of uranium-mine releases and ambient water quality in the Puerco River led to a 4-yr USGS study beginning in July 1988 to describe the chemistry of the Puerco River and its near-channel alluvial water, and to identify the origins of selected radionuclides and other potential contaminants.

Table 1. Selected water-chemistry constituents in the United Nuclear Corporation tailings pond, and tailings solution in the Puerco River on July 16, 1979

Constituents	Concentrations in milligrams per liter	
	Tailings pond [1]	Spill water [2]
Uranium	4.1	6.5
^{226}Radium	[3] 210	[3,4] 100
^{230}Thorium	[3] 10,000	[3] 8,100
Arsenic	0.07	0.008
Sulfate	4,800	27,000
Sodium	520	7,700
Chloride	50	5,500
Chromium	0.15	1.6
Iron	160	2,210
Manganese	14	73
pH [5]	1.9	1.4

[1] Sampled February 5, 1979, from tailings pond (Weimer and others, 1981).

[2] Sample collected by United Nuclear Corporation at bridge over Puerco River at Pinedale, New Mexico, July 16, 1979 (Wirt and others, 1991).

[3] Picocuries per liter.

[4] Dissolved.

[5] Values in pH units.

Research Design

Surface-water chemistry and suspended-sediment concentrations were monitored at nine continuous-record streamflow-gaging stations equipped with telemetry and automatic samplers, and at six partial-record sites equipped with crest-stage gages and passive samplers (Gray and Fisk, 1992). Six of the continuous-record gages monitored flow downstream from the uranium mines, and three monitored flow in basins unaffected by uranium mining that were used as reference sites. Thirty-one monitor wells were installed at six sites in the Puerco River alluvium from near Manuelito, New Mexico, to near Chambers, Arizona. The wells were used to obtain measurements of hydraulic head and water samples for chemical analyses at discrete locations in the aquifer to describe variability in alluvial water chemistry and ground-water flow directions.

Occurrence and Probable Sources of Radionuclides

Van Metre and Gray (1992) estimated that a total of about 560 Mg of uranium and about 310 curies of gross-alpha activity were released by shaft dewatering and the tailings pond spill. The cumulative 22 yr of mine dewatering produced more than 99 percent of the uranium and 85 percent of the gross-alpha activity released to the Puerco River. ^{226}Ra and ^{230}Th accounted for most of the activity in the tailings pond spill. Mass balance estimates indicate that most uranium released did not remain in solution, but was sorbed onto sediments (Van Metre and Gray, 1992).

In 1988-89, a zone of above-background concentrations of dissolved uranium in Puerco River alluvial ground water was discernible as far as 70 km downstream from the mines (Van Metre and Gray, 1992; Wirt, 1993) (fig. 2). Analyses of ground-water samples collected in 1990-91 from near the streambed at several sites had smaller concentrations of dissolved uranium than those detected in 1989, suggesting that water quality was improving. Except for selected locations near the streambed, all ground-water samples collected from the alluvial aquifer downstream from Gallup, New Mexico, met the EPA's proposed MCL

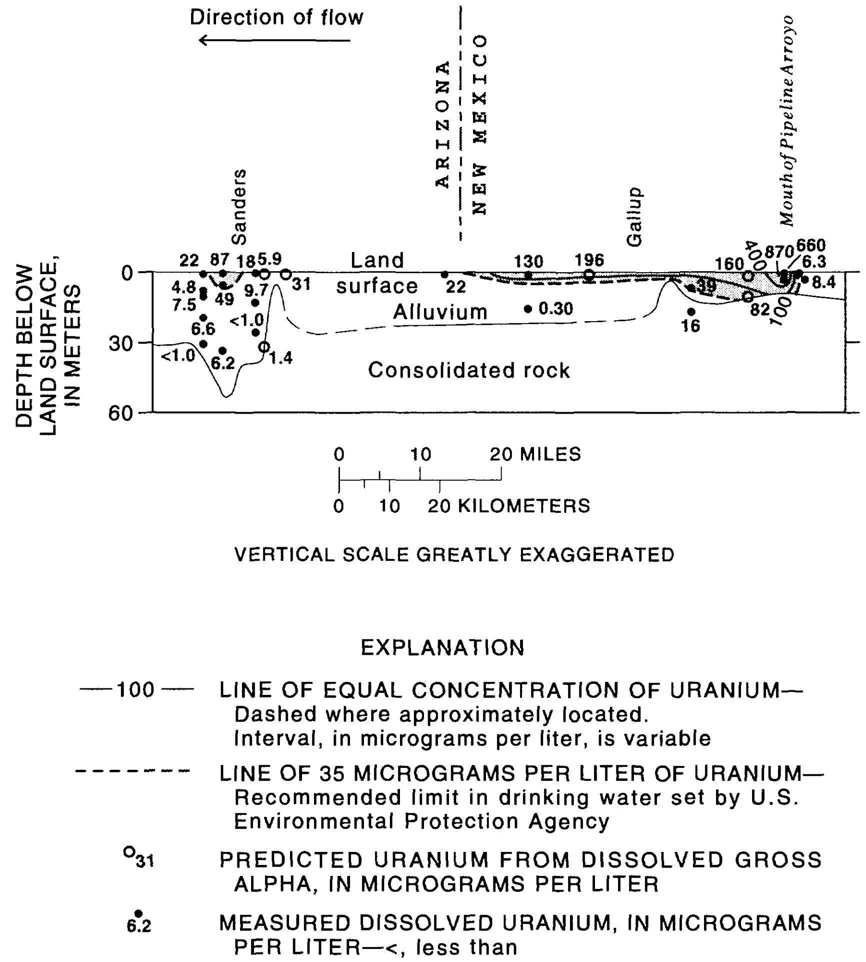

Figure 2. Occurrence of dissolved uranium in the alluvial aquifer that underlies the Puerco River, Arizona and New Mexico. Samples collected between December 1988 and November 1989.

for uranium (U.S. Environmental Protection Agency, 1991), MCL for ^{226}Ra, and State of Arizona MCL for gross-alpha plus gross-beta activity. Only dissolved solids, iron, and manganese commonly were in exceedence of the EPA's secondary MCL for those constituents.

Wirt (1993) used variations in the ratio of ^{234}U to ^{238}U to identify sources of uranium in shallow ground water beneath the Puerco River. Ground water in the basin unaffected by mining has U^{234}/U^{238} values ranging from 1.5 to 2.7. Ratios exceeding unity (secular equilibrium) result from alpha recoil of solid-phase ^{238}U over geologic time causing the ^{234}U daughter to be placed in favorable leaching sites. The range of uranium-isotope ratios calculated for Puerco River alluvial ground water indicates that the above-background concentrations of uranium measured 5 yr after mining operations ceased were principally attributable to mine-dewatering releases.

Samples of unfiltered runoff from 1988-91 at all streamflow-gaging stations typically contained radium and gross-alpha plus gross-beta activities, and concentrations of arsenic, beryllium, cadmium, chromium, calcium, lead, and nickel in exceedence of applicable water-quality standards. Suspended sediment, concentrations which often exceeded 10 percent by weight, typically carried more than 99 percent of the mass of analyzed constituents. The dissolved fraction of runoff monitored at the streamflow gages typically met applicable drinking water-quality standards. Similarities found in the chemistry of suspended sediments between the three reference stream gages and those downstream from the uranium mines led to the conclusion that, in the absence of mining releases, constituent concentrations in runoff reflect those for natural conditions in this mineral-rich region.

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GEOCHEMICAL CHARACTERIZATION OF URANIUM MILL TAILINGS AND RADIONUCLIDE MOBILIZATION PROCESSES

By Edward R. Landa

Introduction

Uranium mill tailings (UMT) represent a voluminous form of low-level radioactive waste generally disposed of in surficial impoundments, with varying degrees of remediation following decommissioning of the mill. Our work has addressed the geochemical forms of radionuclides in these tailings and potential mobilization mechanisms in the hydrosphere. Due to its high radiotoxicity, ^{226}Ra, with a half-life of 1,600 yr, is generally the uranium daughter product of most concern in hazard assessments of water supplies and food chains associated with UMT, and was the target of studies reported here.

The Milling and Aqueous Environments

As previous investigators had shown redistribution of ^{226}Ra between particle size fractions to occur in both acid and alkaline leaching circuits, we investigated the retention of ^{226}Ra by common and minor minerals in uranium ores under simulated acid milling conditions. Uranium-bearing sandstone ore was milled on a laboratory scale with sulfuric acid. At regular time intervals, filtrate from this suspension was placed in contact with mixtures of quartz sand and various potential sorbents which occur as gangue in uranium ores; the potential sorbents included clay minerals, iron and aluminum oxides, feldspar, fluorite, barite, jarosite, coal, and volcanic glass. After equilibration, the quartz sand-sorbent mixtures (mixture ratio 15:1 by weight), referred to here as synthetic substrates (SS), were separated from the filtrate and radioassayed by gamma-spectrometry to determine the quantity ^{226}Ra sorbed.

About 20 to 60 percent of the ^{226}Ra was sorbed by all of the SS, except for the coarse quartz sand alone. There was an approximately five-fold increase in sorption between the 30-40 mesh quartz and the -240 mesh quartz, suggesting that surface area is one of the controlling factors in sorption during milling. As finely divided quartz is undoubtedly a major component in mill-feeds containing quartz-bearing ores, the sorption of radium by such material may explain much of the redistribution of radium to fine particles noted in particle-size studies of uranium mill tailings. The leaching of ^{226}Ra from these SS was then examined using selective extraction techniques. The sequence of extractants and targeted radium hosts are shown in table 2. The ^{226}Ra contents of the SS at the start, and the fractional removals with each extraction are

Table 2. Sequence of solutions used for leaching tests (Landa, 1991)

Sequence number	Solution	Remarks
I 0.005 *M*	H_2SO_4	To simulate the effect of dilute H_2SO_4 as might be encountered at the end of the washing circuit of an acid-leach uranium mill.
II, III	Deionized water	Two extractions in sequence to simulate the effect of further dilution of the sulfuric acid as might be encountered with exposure of tailings to dilute natural waters following disposal.
IV 1.0 *M*	NH_4Cl	The exchangeable and other "easily-extractable" forms of ^{226}Ra as noted by Steger and Legeyt (1987).
V 1.0 *M*	HCl	While the action in step (IV) is displacement of the trace quantities of ^{226}Ra from the surface by ion competition for the same adsorption sites, the solution here does that plus provides acidity to enhance the dissolution of the sorbent surface. Single extractions of this type have often been used to characterize soils and aquatic sediments for biologically available metals.

Table 3. ^{226}Ra concentration of synthetic substrates (SS) after exposure to acid uranium milling liquor and subsequent extraction reported as a percentage of the initial radium concentration (Landa, 1991)

[pCi/g, picocuries per gram]

SS (identified by varying constituent)	^{226}Ra concentration (pCi/g)	I 0.005 *M* H_2SO_4 (percent)	II H_2O-(1) (percent	III H_2O-(2) (percent)	IV 1.0 *M* HCL (percent)	V 1.0 *M* HCL (percent)	Total extraction by summation (percent)
Ottawa sand only	2.0	31	29	10	26	2.0	98
Fine silica	10.	8.5	30	33	26	1.6	99
Potassium feldspar	9.1	4.3	16.5	21	54	4.5	100
Sodium feldspar	20.4	1.2	4.2	14	87	6.8	113
Pyrophyllite	7.2	1.0	8.3	8.2	50	11	79
Kaolinite	6.6	18	34	7.6	48	5.6	113
Bentonite	16.5	0.7	1.6	3.3	97	3.1	106
Bauxite	13.1	3.7	9.8	20	66	5.4	105
Hematite	6.5	10	18	22	55	0.9	106
Magnetite	15.9	1.1	3.5	8.6	94	4.1	111
Barite	22.0	0.08	0.03	0.03	0.03	0.09	0.26
Jarosite	16.5	0.1	1.1	8.2	83	2.2	95
Fluorite	18.8	0.8	0.6	0.7	31	48	81
Volcanic ash	17.3	0.5	2.8	6.9	94	3.7	108
Coal	18.1	0.6	0.9	1.9	88	15	106

shown in table 3. Radium retained by the kaolinite and quartz materials (Ottawa sand only and fine silica) appears to be the most easily desorbed, with about 60-70 percent extracted by the dilute H_2SO_4 and the two sequential deionized water washes. In contrast, the coal-, fluorite-, barite- and bentonite-bearing SS released less than 6 percent of their radium inventory with these three leaches. Significant quantities of gypsum formed during the sorption phase in the fluorspar SS. The lack of radium leaching by either the dilute H_2SO_4 or deionized water here suggests that it is retained in a form other than gypsum. (The solubility of gypsum in 0.005 *M* H_2SO_4 is about the same as in water—about 2.1 g/L at 25 °C (Linke, 1958, p. 663). Alternatively, the radium may occur initially as a gypsum coprecipitate and upon dissolution of the gypsum, the radium may be sorbed by another phase.

Although the 1 *M* NH_4Cl extractant could potentially increase the solubility of sparingly soluble salts such as $BaSO_4$ and $PbSO_4$, which are known to be good sinks for radium (Steger and Legeyt, 1987), the presence of residual sulfate from the sorption stage and from the first extractant in the sequence here will tend to suppress dissolution (Benes and others, 1981). Thus, the large releases of radium seen at this step can probably be attributed solely to ion-exchange reactions. Conversely, the lack of radium leaching seen with the barite SS suggests that the sorbed radium here is nonexchangeable.

The HCl-extractable fraction was generally less than 10 percent, however for the fluorspar-bearing SS it amounted to almost 50 percent. Work at the U.S. Atomic Energy Commission's Winchester Laboratory in the late 1950's (National Lead Co., 1960) showed that radium could be efficiently removed from an acidic (pH 1.8) uranium mill effluent by addition of NaF to precipitate CaF_2. Thus the CaF_2 structure appears capable of including Ra, presumably by substitution into the Ca lattice position. The solubility of CaF_2 is only slightly enhanced in 1 *M* NH_4Cl compared to water (Linke 1958, p. 601, 603); hence the large release of Ra seen in table 2 with NH_4Cl is thought to be due to ion-exchange displacement. However, the solubility of CaF_2 increases by almost two orders of magnitude on going from water to 1.0 *M* HCl (Linke, 1958, p. 601, 602). Hence the HCl leach used here, which released almost 50 percent of the ^{226}Ra in the SS, is thought to cause this action by dissolution of $Ca(Ra)F_2$.

As compared with the other SS tested, the most anomalous behavior was exhibited by the barite SS. While the five-step extraction provided nearly complete recovery of radium for most of the SS, for the barite SS, the recovery was less than 0.5 percent. The desorption pattern of the quartz sand that makes up 94 prcent by weight of the barite SS was completely masked in the mixture due to competition by barite for radium sorption during the earlier exposure to the acid milling liquor and/or resorption by barite of any radium desorbed from the quartz during the five-stage leaching described here. While $BaSO_4$ solubility is significantly enhanced on going from water to 1.0 *M* HCl (Benes and others, 1981), the presence of soluble sulfates will suppress the reaction. This is the probable reason for the lack of radium release seen here with the barite SS. Indeed, Benes and others (1981) used 1.0 *M* HCl spiked with 60 parts per million sulfate to selectively dissolve "acid-soluble" forms of radium and barium (for example, that carried on ferric hydroxide), while preserving radium held as $Ba(Ra)SO_4$. Seeley (1976) reported essentially no desorption of ^{226}Ra by 0.01-1.0 *M* HCl from synthetic tailings in which radium was coprecipitated with $BaSO_4$ onto quartz sand.

In the present study, the radium is sorbed onto preformed barite crystals rather than being coprecipitated from solution. However it is likely that during the sorption period, the radium initially retained by the exchange of ions between the solution and those composing the surface of the crystal is slowly incorporated into the crystal lattice during recrystallization of the barite. Such a recrystallization process would be enhanced by the elevated temperature at which the sorption took place. The final product would thus resemble a $Ba(Ra)SO_4$ coprecipitate, except that the radium would occur only in the outer rind of the barite particles. A microautoradiographic study of uranium mill tailings from Monticello, Utah, by Stieff (1985), showed particles which were tentatively identified on the basis of birefringence and high relief as barites, which were loci for elevated concentrations of ^{226}Ra. The resistance to NaCl and HCl leaching shown here for radium sorbed on barite may help to explain a part of the unextractable, refractory fraction observed during investigations (Ryon and others, 1977; Levins and others, 1978) of the use of electrolytes and acids in remedial action and novel milling schemes aimed at reducing the radium contents of tailings to levels below regulatory concern.

The important role of alkaline earth sulfates in the retention of ^{226}Ra and other radionuclides in acid-milled uranium tailings is supported by other recent investigations. Morrison and Cahn (1991) examined acid-leached tailings from several mills which used Colorado Plateau sandstone ores, and found most of the alpha activity was associated with barium-strontium sulfate grains. Alpha-track maps of polished thin sections showed both grains with uniform track densities, as might happen with coprecipitation, and grains with only alpha-tracked rims, indicative of sorption. From a purely analytical chemistry point-of-view, the insolubility of $BaSO_4$ ($K_{sp} = 1.08 \times 10^{-10}$ at 25 °C) might lead one to believe radium coprecipitated with $BaSO_4$ to be very immobile. However Landa and others (1986) showed that ^{226}Ra leaching from UMT was greatly enhanced in the presence of sulfate-reducing bacteria (fig. 3). These bacteria were isolated in low numbers from tailings samples, but were isolated in relatively high numbers in organic matter-rich cover soils used in tailings reclamation and revegetation (Miller and others, 1987). The observed radium release to solution did not appear to be due to chelates excreted by the bacteria, but rather was probably due to the microbially-mediated dissolution of barite and similar phases in the tailings. A similar effect was later demonstrated with iron (III) - reducing bacteria, which do not reduce sulfate (Landa and others, 1991). The action of these microorganisms in dissolving ferric hydrous oxide phases in UMT results in the release of ^{226}Ra to solution (fig. 3). These findings suggest that engineering measures or natural forces which place UMT in anaerobic environments may enhance the release and transport of ^{226}Ra. Eberl and Landa (1985) showed that clay minerals also enhance the dissolution of $BaSO_4$, $SrSO_4$, and the release of ^{226}Ra from UMT, presumably by acting as sinks for cations (Ba^{++}, Sr^{++}, Ra^{++})

The action of similar anaerobic microorganisms can be exploited at active mining and milling sites, and in remedial action programs. For example it may be possible to use microbial reduction of uranium to treat mine drainage water for uranium removal. The soluble oxidized form of uranium, U^{6+}, is reduced by some anaerobic bacteria to insoluble U^{4+}, which precipitates as uraninite (Lovley and others, 1991; Gorby and Lovley, 1992). The process was not inhibited by low pH (pH 4.0), nor relatively high concentrations of copper (4.5 µM), zinc (85 µM), or other trace metals in a uranium mine drainage water. However, copper (either Cu^{+} or Cu^{++}) at 100 µM (6,350 $\mu g \cdot L^{-1}$) was inhibitory to U^{6+} reduction (Lovley and Phillips, 1992). By combining an initial bicarbonate extraction with a microbial step, it may be possible to decontaminate soils containing uranium in a variety of forms including ore, mill tailings, and uranium-bearing, armor-piercing, munitions alloys (Lovley and others, 1992).

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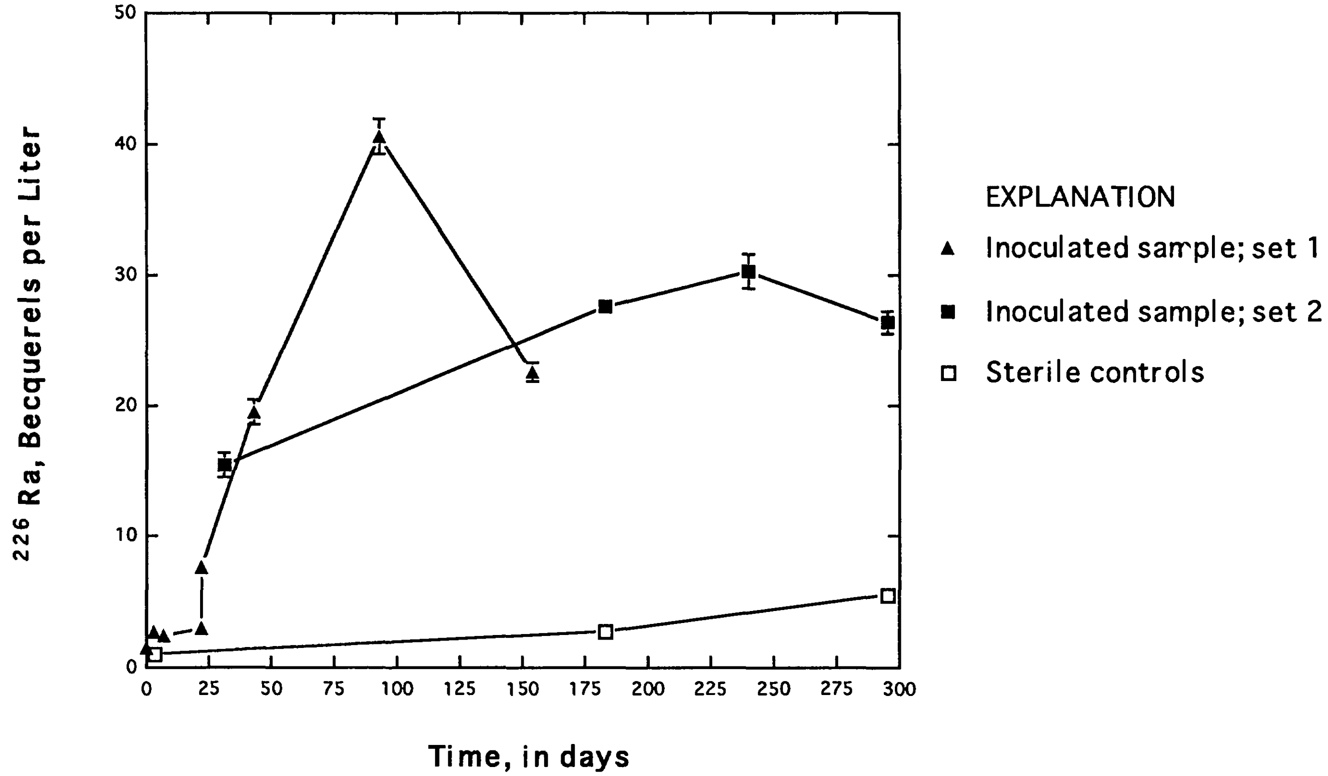

Figure 3. Soluble ^{226} Ra in uranium mill trailings and media inoculated with *shewanella putrefaciens* and in sterile uninucleate controls.

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ISSUES ASSOCIATED WITH RADIOLOGICAL CONTAMINANT TRANSPORT AT DECOMMISSIONING SITES

By Rateb (Boby) Abu-Eid, Jack P. Parrott, M. (Sam) Nalluswami, *and* Michael Weber

Introduction

The United States Nuclear Regulatory Commission (NRC) staff has been involved in various activities associated with decommissioning of radiologically contaminated sites. These activities have included; site characterization, investigation of the extent of contamination, and assessment of potential radiological impacts using transport pathway analysis and modeling approaches. In the course of performing these activities, NRC staff has encountered some previously unaddressed technical issues that required either developing new technical guidance or conducting additional technical studies and investigations to ensure that appropriate and adequate resolutions to these issues were achieved. The major technical issues encountered were: (1) Selection and determination of the retardation factors; (2) classification of uranium in soil as soluble or insoluble; and (3) selection and use of contaminant transport codes.

Selection and Determination of the Retardation Factors:

The retardation factor (R_d) is commonly expressed, using the Freundlich isotherm (Freundlich, 1926), in terms of its linear relationship with the distribution coefficient (K_d). Thus, doubling the K_d value halves the radionuclide migration velocity in relation to the ground water velocity. Therefore, the importance of the accurate determination of the K_d cannot be overemphasized in calculation of the velocity of radionuclide movement in subsurface geological materials. The major technical issues associated with the retardation factor are:

1. The limitations of the current laboratory methods used for K_d determinations

Currently, there are no adequate and reliable common approaches or methods for selection and/or determination of the K_d parameter for decommissioning sites. The most common K_d determination methods currently being applied at decommissioning sites are: American Society for Testing and Materials (ASTM) D 4319-83 (ASTM, 1983), and ASTM D 4646-87 (ASTM, 1987). A third ASTM method (ASTM D4874-89; ASTM, 1989) is also used although it is not specifically dedicated to K_d determination. These methods have the following shortcomings:

(a) Although the overall precision and reproducibility of these methods are reported to be in the range 10-25 percent, the actual output results reported by licensees are much larger. Table 4 shows examples of average K_d values, standard deviations of the values, and the relative standard deviations of the K_d's, obtained for some soil samples and conducted under similar conditions. As can be noted, the relative standard deviation of the values, empirically determined for decommissioning sites, fall in the range 20-100 percent of the average K_d values.

(b) The methods call for removal of organic matter from the sample. Since organic matter influences the retardation potential of the soil, the result may not be representative of actual soil conditions.

(c) The methods allow for alternating moisture content through drying and sample preparations. Since K_d is largely dependent on the soil/water ratio, results determined in the laboratory may be substantially different from those found on the site.

(d) The methods allow for using intrusion water (contaminated water from onsite) as the solution medium. It is preferable, however, to use clean ground water from the site rather than contaminated water since the latter may contain some dissolved contaminants and therefore may not accommodate as much dissolved radionuclide as the clean ground water.

Table 4. Average K_d values, standard deviations, and relative standard deviations empirically determined for decommissioning sites
[Th, thorium; U, uranium; mL/g, milliliters per gram]

Radionuclide	Number of runs	Average KdM (mL/g)	Standard deviation (σ_n)	(σ_n/M) × 100
^{232}U	5	1680	986	59
^{228}Th	5	4552	1407	31
^{232}U	5	1121	726	65
^{228}Th	5	3849	1079	28
^{238}U	20	18047	18078	100
^{238}U	15	1242	966	78
^{238}U	7	2427	1638	68
^{238}U	7	3383	685	20

2. Wide range of K_d values reported in the literature for the same radionuclide

Some licensees and transport analysts select retardation coefficient values reported in the literature. In most cases these selected values do not represent site specific conditions and fall within a wide range since they were derived under various physical and chemical conditions. Sheppard and Thibault (1990) and Sheppard and others (1991) reported ranges of K_d values for four common type of soils; sandy, clayey, loamy, and organic soils. The K_d values presented by these authors indicated that random selection of K_d values from the literature, without matching site specific conditions, could produce a difference in the retardation factor of 1 to 6 orders of magnitude from the actual values.

3. Use of nonconservative default K_d's embedded in transport pathway analysis codes

Certain transport codes, specifically those codes that couple contaminant transport modeling with radiological impact assessments, adopt default K_d parameters that are widely different and may not represent site specific conditions. Table 5 lists examples of default K_d's for codes used by NRC staff (for example, RESRAD (Gilbert and others, 1989) and NUREG/CR-5512 (Kennedy and Strenge, 1992). The default K_d's for RESRAD code, for example, represent values corresponding to silt/clay soil type which are not considered conservative, specifically if the site contains sandy soil. Table 5 also presents average K_d values reported by Sheppard and Thibault (1990). K_d values for sandy soil reported in Table E.3 of RESRAD manual (Gilbert and others, 1989) are also shown for comparison.

Table 5.—Comparison of "K_d" default values used in radionuclide transport codes with values quoted in the literature

[---, data not available]

Radionuclide	Sheppard and Thibault (1990)	NUREG/CR-5512	RESRAD (Table E.3)	RESRAD defaults
Actinium	450	417	20	20
Americium	1,900	1,887	---	20
Bismuth	100	118	---	600
Cobalt	60	59	100	1,000
Cesium	280	270	80	500
Hydrogen	0.06	1.25	0.0	0.0
Potassium	15	18	---	5
Protactinium	550	526	---	50
Lead	270	270	10	100
Plutonium	550	555	200	2,000
Radium	500	500	7	70
Strontium	15	10	3	30
Technetium	0.1	0.1	---	0.0
Thorium	3,200	3,226	6,000	60,000
Uranium	35	15	5	50

4. Field methods of K_d determination:

In some cases licensees analyze core samples of saturated soil and contaminated ground water, the ratio of radionuclide concentration in soil to ground water is calculated then to estimate K_d values. Using this method, it is assumed that equilibrium has been reached and dilution effect, due to non-contaminated ground water flow, is insignificant.

5. Calculation of K_d Value From Soil-to-Plant Concentration Ratio (CR):

This method is used to derive the distribution coefficient using soil-to-plant effective concentration ratios Martin and Bloom (1980) and a generically derived equation which employs concentration factors to calculate K_d's for four type of soils (Baes and others, 1984 a, b). This method is inaccurate due to the dependance of plant uptake on type of soil, type of plant, and location and distribution of contaminants within the root zone.

In summary, from the above review, the current methods and procedures employed in K_d selection or determination are expected to produce uncertainties in K_d values up to 100 percent or more. Therefore, these methods need to be developed and revised to reduce these large uncertainties. NRC staff also stresses the importance of determining K_d's based on site specific conditions and caution using the default K_d values in the models or codes regardless of the actual site specific conditions.

Characterization of Uranium Solubility in Soil

NRC's existing guidance on decommissioning criteria for soils and other materials contaminated with uranium and thorium is contained in a 1981 Branch Technical position (BTP) entitled "Disposal or Onsite Storage of Thorium or Uranium Wastes from Past Operations." Under Option 2 of the BTP, two different sets of criteria are provided for soluble and insoluble uranium that has been enriched and depleted with respect to ^{235}U. Although NRC has a rulemaking underway that is expected to eventually replace the criteria in the 1981 BTP, this rulemaking will not be completed until at least 1995. In the interim, NRC will continue to require licensees and responsible parties to decommission facilities having soil contaminated by uranium and/or thorium in accordance with the criteria in the BTP. These criteria focus on the solubility of uranium within the human body (that is, lung fluid), which is determined primarily by the chemical form of the uranium. To date, acceptable procedures are not available for determining the environmental availability of uranium in soil even though this can have a large impact on remediation costs, environmental migration, and doses to humans. The current method accepted for determination of uranium solubility is the NRC NUREG/CR-1428 (Kalkwarf, 1980) which is only applicable to solubilities of airborne uranium particulate. The method requires determination of the rates at which uranium particulate dissolve in simulated lung fluid media. This method is lengthy and requires months to reach dissolution equilibrium. Currently NRC staff is conducting investigations to justify using one of the following two approaches:

1. Direct determination of uranium solubility in soil using a modified procedure from the simulated lung fluid procedure that is applicable for contaminated soils in the decommissioning sites.
2. Indirect Procedure by identifying and quantifying uranium compounds in soils and estimating their solubilities based on available solubility data for such compounds.

This issue has been formulated in a proposed research project for future implementation to achieve an appropriate resolution on the issue of uranium solubility.

Selection and Use of Contaminant Transport Codes

Most of contaminant transport codes currently used by NRC staff depend largely on pathway analysis of contaminant releases, coupled with radiological impacts assessment of dose or risk to a critical member of the public or risk, to the surrounding population within 50 mi of the site. The codes selected in many cases do not contain adequate transport parameters and formulation. as typically required in ground-water modeling (Mercer and Faust, 1981). This is due to the fact that radiological impact assessors prefer to use simple and highly conservative codes to ensure that actual risk or hazards have been accounted for. Some codes used do contain basic transport elements without appropriate analysis to account for site specific conditions. Selection of the appropriate code that serves the purpose of analysis represents a serious difficulty. Thus, frequently, simple screening codes are commonly used to simulate complex contaminant transport conditions or complex 3-D codes are used to simulate site conditions where contaminant transport is of meager significance. Finally, NRC staff is faced with the dilemma of receiving mixed signals (in the published literature) on the issue of whether or not groundwater codes can be validated (for example, Konikow and Bredehoeft, 1992; Tsang, 1991). This issue needs to be addressed by modelers to achieve a uniform approach to ground water codes and model validation.

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REDUCTIVE PRECIPITATION OF URANIUM BY MICROORGANISMS—AN OVERVIEW

By Derek R. Lovley

Introduction

Microbial reduction of soluble U(VI) to insoluble U(IV) may be an important process in the global uranium cycle and may also be a useful technique for removing uranium from contaminated environments (Gorby and Lovley, 1992; Lovley and Phillips, 1992; Lovley and Phillips, 1992; Lovley and others, 1991). The purpose of this paper is to review what is known about microbial reduction of U(VI) in sedimentary environments.

U(VI)-Reducing Microorganisms

Geobacter metallireducens (formerly known as strain GS-15) was the first organism found to use U(VI) as a terminal electron acceptor (Lovley and others, 1991). *G. metallireducens* grows by carrying out the reaction:

$$\text{acetate}^- + 4\,U(VI) + 4\,H_2O \rightarrow 2HCO_3^- + 4\,U(IV) + 9H^+.$$

Shewanella putrefaciens can also grow with U(VI) as the sole electron acceptor and H_2 as the electron donor:

$$H_2 + U(VI) \rightarrow 2H^+ + U(IV).$$

Both organisms will grow in high (8 m*M*) dissolved uranium.

Several *Desulfovibrio* species including *D. desulfuricans* and *D. vulgaris*, can also enzymatically reduce U(VI) with either H_2 or lactate (Lovley and Phillips, 1992; Lovley, Roden, and others, 1993). However, attempts to grow these organisms with U(VI) as the sole electron acceptor were unsuccessful (Lovley and Phillips, 1992).

Enzymatic Mechanisms for U(VI) Reduction

The enzymatic mechanisms for U(VI) reduction by *G. metallireducens* and *S. putrefaciens* are ill-defined. The fact that these organisms conserve energy to support growth by oxidizing nonfermentable substrates with U(VI) as the sole electron acceptor suggests that electron transport-linked phosphorylation must be involved. Electron transport to or through a *c*-type cytochrome is likely, based on the observation that U(VI) oxidizes the *c*-type cytochromes in whole cells of *G. metallireducens* (Lovley, Giovannoni, and others, 1993).

However, a U(VI) reductase has been isolated from the U(VI) reducer *D. vulgaris* (Lovley and others, 1993). The soluble fraction of *D. vulgaris* rapidly reduces U(VI) with H_2 as the electron donor. If cytochrome c_3 is removed from the soluble fraction of *D. vulgaris*, then all capacity for U(VI) reduction is lost. If cytochrome c_3 is added back, then the capacity for U(VI) reduction is restored. U(VI) rapidly oxidizes previously reduced cytochrome c_3. U(VI) is rapidly reduced when c_3 is combined with hydrogenase, the physiological electron donor for c_3, and H_2.

Environmental Significance of Microbial U(VI) Reduction

The environmental significance of microbial U(VI) reduction is that U(VI) is highly soluble in most natural waters, whereas U(IV) is highly insoluble (Langmuir, 1978). The reduction of U(VI) to U(IV) in anaerobic marine sediments is, globally, the most significant sink for dissolved uranium (Anderson and others, 1989; Klinkhammer and Palmer, 1991; Veeh, 1967). The reductive precipitation of uranium from ground water is considered to be the mechanism for the formation of some sandstone or roll-type uranium ores (Hostetler and Garrels, 1962; Jensen, 1958; Langmuir, 1978). Although the earlier geochemical literature (Hostetler and Garrels, 1962; Jensen, 1958; Langmuir, 1978) suggested that U(VI) reduction in anaerobic environments was the result of nonenzymatic reduction of U(VI) reduction by sulfide or H_2, neither are effective U(VI) reductants at the temperatures and pH typical of aquatic sediments or ground water (Lovley and others, 1991). Sterilization of anaerobic sediments inhibits U(VI) reduction (Lovley and others, 1991). These findings suggest that U(VI)-reducing enzymes are responsible for U(VI) reduction in these environments.

Microbial U(VI) reduction may be used to remove uranium from contaminated waters and soils. In most natural surface and ground waters, U(VI) is in the form of uranyl-carbonate complexes (Langmuir, 1978). Furthermore, uranyl-carbonate complexes are the typical dissolved uranium form that results from a variety of man's activities with uranium (Lovley and Phillips, 1992). Studies with *G. metallireducens* (Gorby and Lovley, 1992) and *D. desulfuricans* (Lovley and Phillips, 1992) demonstrated that U(VI)-reducing microorganisms can reduce the U(VI) in U(VI)-carbonate complexes. The U(IV) precipitates as uraninite (UO_2). All of the uraninite precipitate is extracellular. Thus, microbial uranium reduction has the potential to take uranium that is dispersed in a large volume of liquid and concentrate it to a very pure, compact solid.

D. desulfuricans was chosen for detailed studies on microbial removal of U(VI) from contaminated environments because of the ease in mass culturing this organism and because its U(VI)-reducing capacity is extremely stable. For example, freeze-dried cells kept under air at room temperature lose none of their potential for U(VI) reduction even after 6 months of storage (Lovley and Phillips, 1992). *D. desulfuricans* effectively reduces U(VI) both at very high (24 m*M*) and at relatively low (> 50 n*M*) concentrations (Lovley and Phillips, 1992). Of a wide variety of potentially inhibiting anions and cations that were evaluated, only exceptionally high concentrations (> 20 µ*M*) of copper inhibited U(VI) reduction. *D. desulfuricans* readily removed soluble U(VI) from several mine drainage waters and contaminated ground waters from a U.S. Department of Energy site.

In addition to treating uranium contaminated waters, microbial uranium reduction can be used as part of a technique to concentrate uranium from contaminated soils (D.R. Lovley, E.J.P. Phillips, and E.P. Landa, written commun., 1993). In this process uranium is leached from the soils with a bicarbonate solution and then microbial U(VI) reduction precipitates the uranium from the extract.

Microbial U(VI) reduction has a number of advantages over other previously proposed treatment techniques (Lovley and Phillips, 1992). Advantages include: (1) the ability to precipitate uranium from U(VI)-carbonate complexes; (2) the recovery of uranium in a highly concentrated and pure form; (3) high uranium removal per amount of biomass; (4) the potential to simultaneously treat organic contaminants and uranium by using the organic as an an electron donor for U(VI) reduction; and (5) the potential for in situ remediation of both ground water and surface waters.

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PARTICULATE, COLLOIDAL, AND SOLUTION PHASE ASSOCIATIONS OF PLUTONIUM, AMERICIUM, AND URANIUM IN SURFACE AND GROUND WATER AT THE ROCKY FLATS PLANT, COLORADO

By Richard A. Harnish, Diane M. McKnight, James. F. Ranville, V. Cory Stephens, Bruce D. Honeyman, *and* Scott R. Grace

Introduction

With the cessation of plutonium processing at the U.S. Department of Energy administered Rocky Flats Plant near Denver, Colorado, the focus of activities at the facility has switched to contaminant assessment and identification of potential remediation strategies. In this context we began a study in 1991 to determine the potential for colloid-facilitated transport of the actinides plutonium, americium, and uranium in surface and ground water at the site.

Suspended particles and colloids are important in most natural waters for transport, bioavailability, and reactivity of contaminants. Colloidal particles, those particles generally greater than 1 nanometer and less than a micrometer in diameter, are an especially important component because of their high specific surface areas (which facilitate reactions between solids and solution), and their small size (which inhibits settling and allows them to remain suspended for long periods). Because the term "colloidal" indicates only a size classification, the chemical composition and reactivity of colloids in natural waters is varied. Organic colloidal forms include cellular exudates, and partially to extensively degraded detrital material that may be associated with mineral phases (Ranville and others, 1991). Inorganic forms include clays and insoluble metal oxides. Colloidal particles have been observed in ground waters (Degueldre and others, 1989; Salbu and others, 1985) and have been shown to be mobile in aquifers (Harvey and others, 1989). Association between contaminants with low solubility values and ground water colloids is expected to greatly affect contaminant transport (McCarthy and Zachara, 1989; Penrose and others, 1990). Several studies have shown the importance of this process in radionuclide transport (Buddemeier and Hunt, 1988; Penrose and others, 1990). To significantly alter contaminant transport, colloids must be (1) reactive with the contaminant of concern, (2) stable in the geochemical environment, and (3) present in sufficient quantity (Puls, 1992). The first criterion formed the basis for a preliminary study of the extent of association of the actinides plutonium, americium, and uranium with particles (and in particular colloidal particles) in one ground water and two surface water samples from the Rocky Flats Plant.

The Rocky Flats Plant is located east of the front range of the Rocky Mountains about 16 mi northwest of downtown Denver (fig. 4). The plant opened in 1952, and from this time until plutonium operations were suspended in 1990, it served as a manufacturing facility for plutonium and uranium components and in the processing of retired weapons for plutonium recovery. In the decade from 1958 to 1968, over 5,200 barrels containing actinide-contaminated solvents and cutting oils were stored in an area now known as the 903 pad area. Before their removal, corrosion and leakage of the barrels resulted in surface soil contamination of the immediate area with plutonium, americium, and uranium. Subsequent wind events redistributed the contaminated soil to the east-southeast. It is in this area of surface soil contamination that we sampled one ground water well (designated Well 1587) and two surface water seeps (designated SW-51 and SW-53)

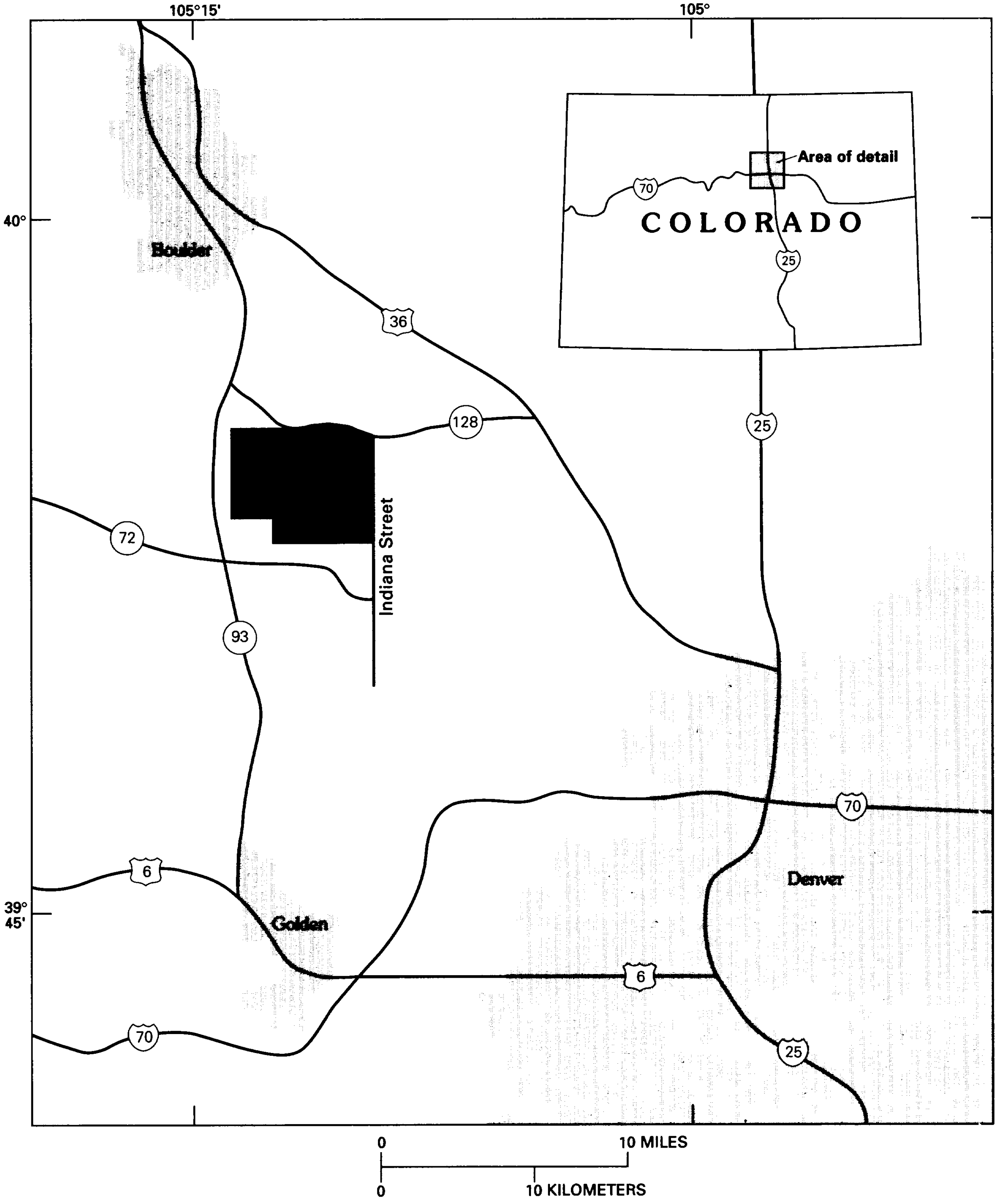

Figure 4. Map showing location of Rocky Flats Plant.

In 1991, pursuant to the Department of Energy's environmental restoration program for the Rocky Flats Plant, and in cooperation with the Department of Energy, the U.S. Geological Survey began a study of the potential for facilitated transport of plutonium, americium, and uranium by colloidal size particles in surface- and ground water at the site. Initial results of this study described here address two purposes: (1) determination of the distribution of plutonium, americium, and uranium among particulate, colloidal, and dissolved phases, and (2) an initial assessment of the chemistry and mineralogy of isolated particulate and colloidal material. This research was supported through an interagency agreement with the Department of Energy (DE-A123-91RF000012). This paper does not necessarily reflect the views of the Department of Energy and no official endorsement should be inferred.

Methods

Study Site

Well 1587 is a shallow alluvial monitoring well located about 100 m east of the 903 pad. SW-51 and SW-53 are surface water seeps that form where ground depressions occur. SW-51 is a shallow stream that empties into a drainage ditch at the perimeter of the 903 pad area; SW-53 is a marshy area about 300 m east-southeast of the 903 pad (fig. 5). All of these waters are well-buffered, neutral to slightly alkaline, calcium/magnesium type waters. The pH ranges from 7.1 at well 1587 to 7.7 and 7.5 at SW-51 and SW-53 respectively.

Sample Collection and Filtration

A 630 liter (L) ground-water sample was collected from well 1587 by using a peristaltic pump. To minimize shear-induced detachment of sorbed particles and resuspension of settled particles in the aquifer matrix, the pumping rate was maintained below 280 milliliters per minute for the duration of sampling. Specific conductance, pH, Eh, dissolved oxygen, temperature, turbidity, and drawdown were monitored during initial purging of the well as a check on sufficiency of purging, and during sample collection as a check on constancy of sample composition. Sample collection was begun when these parameters stabilized. For the surface waters SW-51 and SW-53, 300 L and 120 L were sampled, respectively, with the expectation that particle concentrations would be higher in these surface waters. In all cases, samples were kept at ambient water temperature. The ground-water sample was kept under subdued light. On-site processing of the samples was begun within several hours of sample acquisition, and was continuous upon collection.

Particulate and colloid samples were isolated using the techniques of spiral-flow filtration and cross-flow ultrafiltration. An Amicon spiral-flow ultrafiltration unit with 90-mm diameter, 5.0 µm pore size polycarbonate membrane filter was used for initial sample filtration and collection of the particle fraction greater than 5.0 µm. For subsequent filtration steps, three Millipore Pelicon filtration systems were used in series to collect (1) the fraction between 5 µm and 0.45 µm, (2) the fraction between 0.45 µm and 100,000 Daltons, and (3) the fraction between 100,000 Daltons and 10,000 Daltons. The particles obtained by filtration represent discreet size fractions in what is actually a continuum of particle sizes that range from less than a nanometer up to millimeters in natural systems (fig. 6). For the present study, "particulates" are defined as all those particles retained by the 0.45 µm and 5.0 µm filters; "colloids" are defined as those particles between about 1 nm and 450 nm in size that are retained on 10,000 Dalton and 100,000

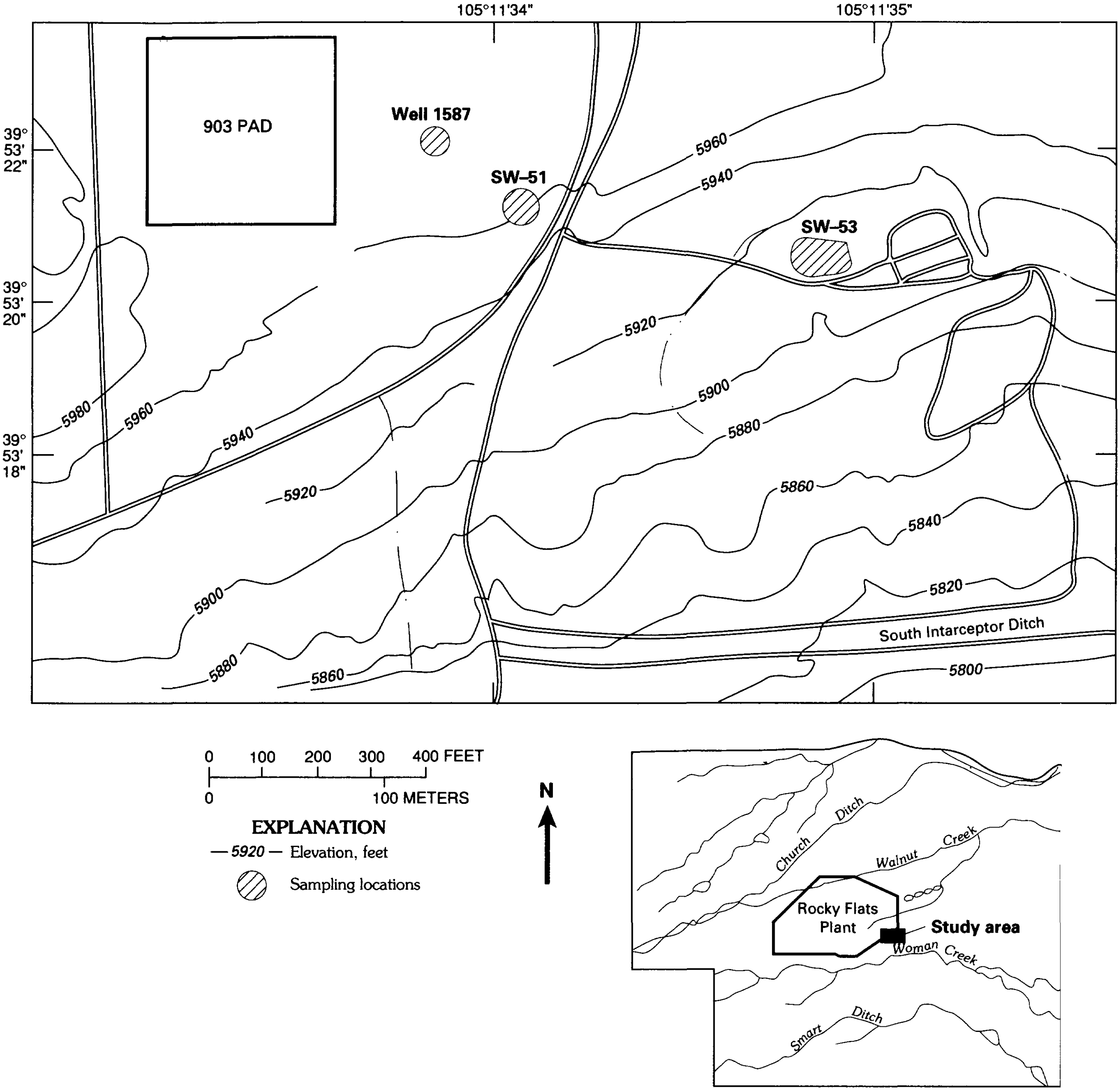

Figure 5. Location of study area indicating sampling sites.

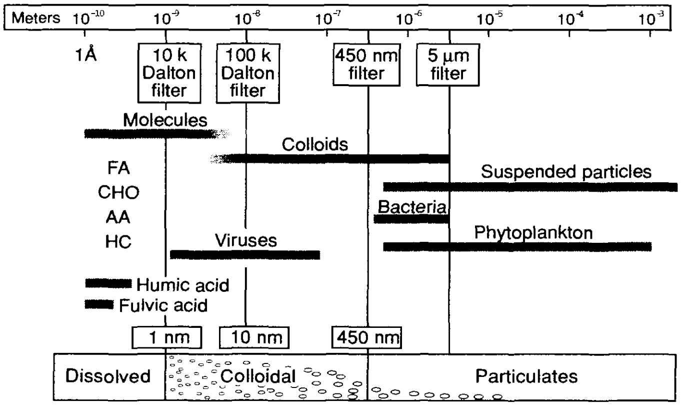

Figure 6. Size classification of aquatic particles.

Dalton filters. Phases that pass through the 10,000 Dalton filters are defined here as "dissolved." For each sample, a portion of the 10,000 Dalton filtrate was extracted using the macroporous nonionic sorbent XAD-8 to isolate humic substances from the dissolved fraction.

Sample Analysis

Lyophilized particle isolates, filter digests, and filtrate samples were analyzed by alpha isotopic separation using an alpha spectrometric detector for ^{239}Pu , ^{240}Pu, ^{241}Am, ^{233}U and ^{234}U. Metals analysis (by inductively coupled plasma-atomic emission spectrometry), organic carbon analysis (by high temperature catalyzed combustion), and scanning electron microscopy-energy dispersive x-ray analysis were also performed on subsamples of the particle isolates and on the various filtrate fractions for particle characterization.

Results and Discussions

Actinide Activity and Particle Mass Distributions

Results of actinide activity analyses, total particle concentrations, and particle mass distributions for samples from well 1587, SW-51, and SW-53 are shown in figures 7-9 respectively. For the well 1587 sample (fig. 7), the total particle concentration was very low (1.4 mg/L), and colloidal size particles comprised a significant percentage (70 percent) of the total particle mass of particles isolated from this sample. Particles greater than 0.45 µm in size made up 30 percent of the particle mass. Results of actinide activity distribution analyses show that ^{239}Pu and ^{240}Pu were associated predominantly with the particulate fraction greater than 0.45 µm (92 percent of total plutonium activity); only 4 percent of plutonium activity was measured in the colloidal fraction, and 4 percent in the dissolved fraction. In contrast, the bulk of ^{241}Am activity was associated with the dissolved fraction; of the remainder,

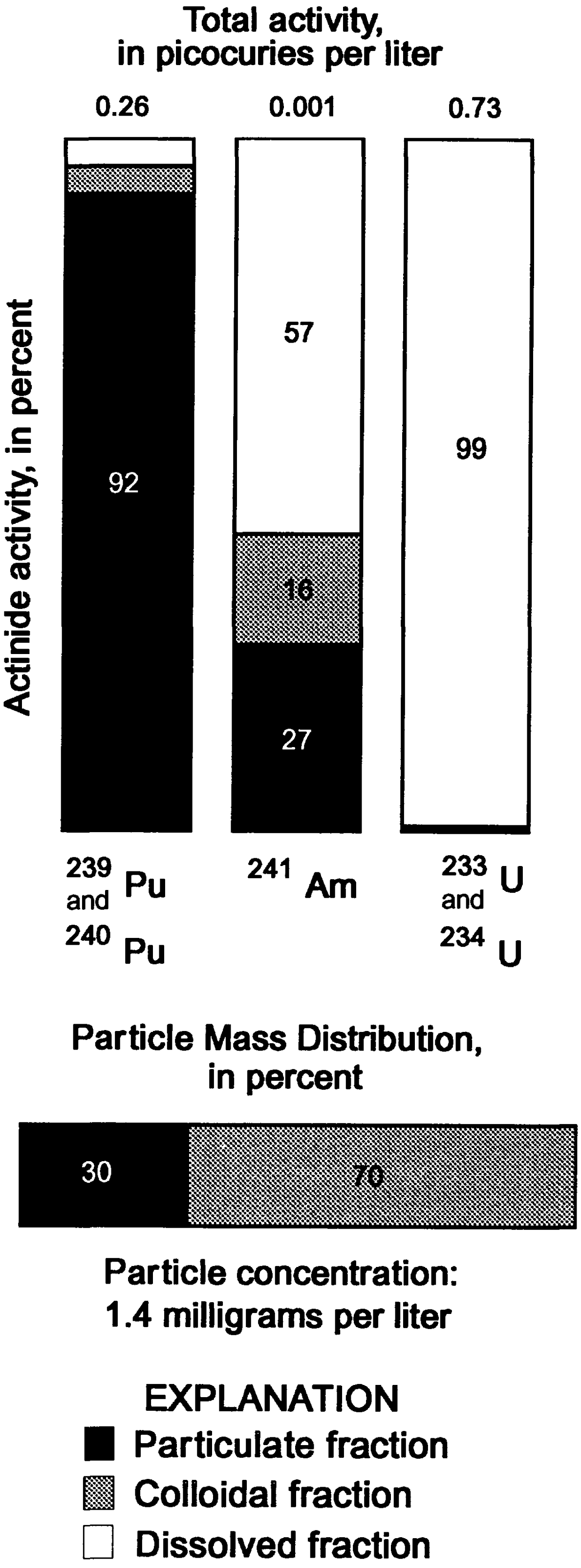

Figure 7. Actinide activity (top three bars) and particle mass (bottom bar) distribution: well 1587 ground water.

27 percent was found in the particulate fraction and 16 percent was associated with colloidal particles. For ^{233}U and ^{234}U, over 99 percent of the total sample activity was in the dissolved fraction.

In the stream water sample SW-51 (fig. 8), the particle mass distribution was similar to that of the ground water sample, but with a higher total particle concentration of 5 mg/L. Particulates made up 32 percent of the total mass of particles, colloids 68 percent. ^{239}Pu and ^{240}Pu were predominantly associated with the particulate fraction (85 percent), with 11 percent of the total activity in the colloidal fraction, and a small percentage in the dissolved fraction. For americium, the majority of the activity (56 percent) was found in the particulate fraction, but there also existed a significant colloidal component (23 percent) and dissolved component (20 percent). As was the case for the ground water sample, ^{233}U and ^{234}U activities were associated almost exclusively with the dissolved fraction.

For the wetland surface water SW-53 (fig. 9) there was a clear difference in particle mass distribution as compared to the well 1587 and SW-51 samples. At SW-53 the particle mass was distributed principally in the particulate fraction, only 11 percent of the total particle mass existed as colloidal size particles. Further, the total particle mass was much higher (103 mg/L) than in the ground water or the other seep. Plutonium activity was concentrated in the particulate fraction. Similarly, almost all of the americium activity was associated with the particulate fraction. The colloidal and dissolved forms measured in the ground water and the other surface seep were essentially absent here. As it was in the other waters examined, ^{233}U and ^{234}U activities at SW-53 were associated almost totally with the dissolved fraction.

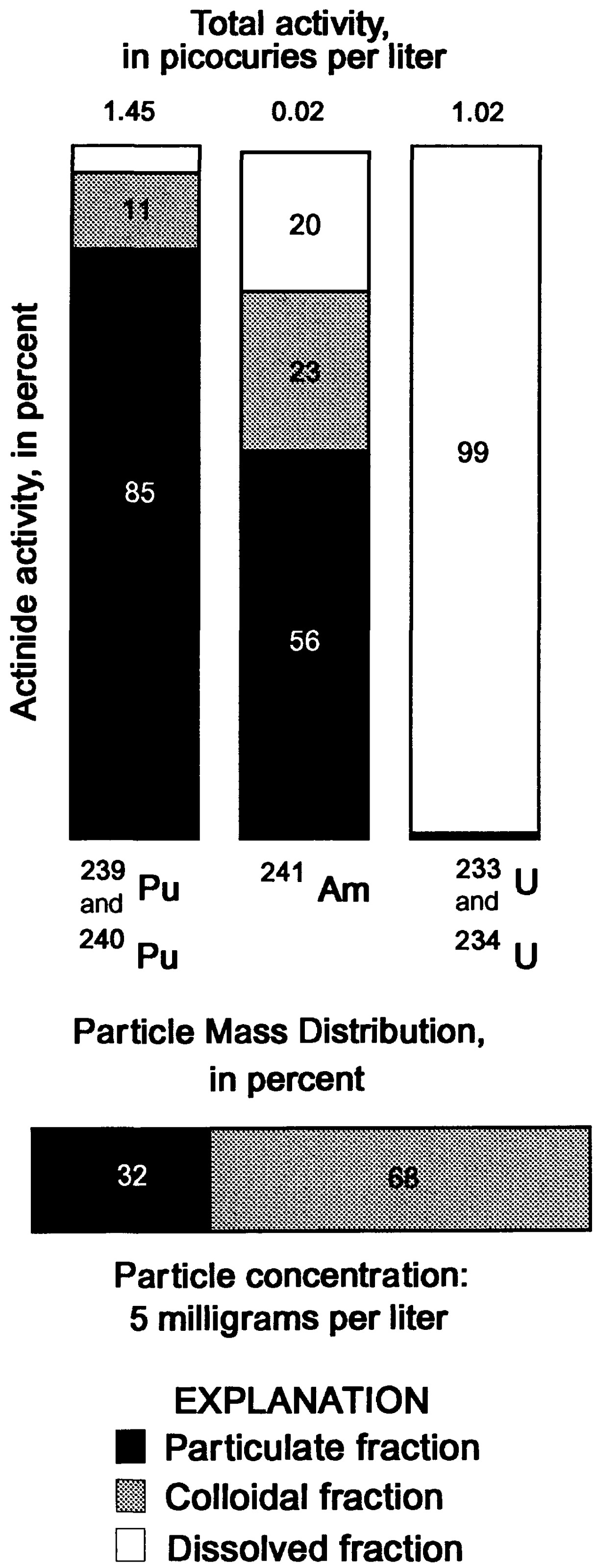

Figure 8. Actinide activity (top three bars) and particle mass (bottom bar) distribution: SW-51 surface water.

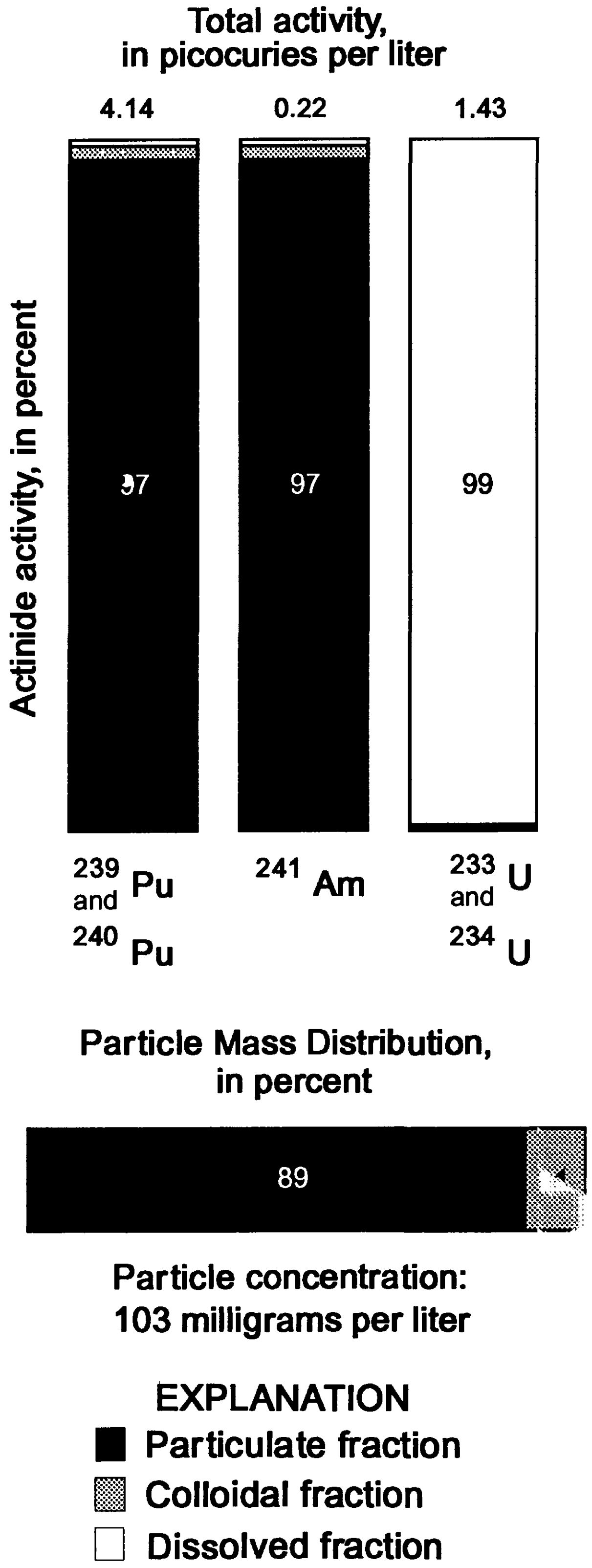

Figure 9. Actinide activity (top three bars) and particle mass (bottom bar) distribution: SW-53 surface water.

To summarize plutonium activity distributions at the three sample sites, three main features are apparent. First, plutonium activities were very low overall, and activities are higher in the surface waters than in the ground water. Second, particulate-associated plutonium was by far the dominant form of plutonium at all three sites: only in SW-51 did colloidal plutonium exceed 10 percent of total plutonium activity. Third, plutonium size distribution appears to be insensitive to particle mass distribution. For example, in the ground water of well 1587, where colloids contributed 70 percent of the total mass of particles, only 4 percent of the plutonium activity was associated with the colloidal fraction. Similarly, although particulates made up only 30 percent of the total particle mass, 92 percent of the plutonium activity was associated with particulates. Similar patterns appear in the samples from SW-51 and SW-53.

For americium, the total activity in these waters was also very low, and americium activity was one to two orders of magnitude lower in the ground water than in the surface waters sampled. In terms of activity distribution there was a clear indication that americium was associated with colloidal and dissolved forms in the ground water and at surface seep SW-51. In SW-53, americium distribution was dominated by particulate forms. These data suggest that americium size association is more sensitive than plutonium to particle mass distribution. At well 1587 and at surface seep SW-51, each with significant percentages of particle mass residing in the colloidal fraction, significant americium activity was found in this fraction. For SW-53, where most of the particle mass was in the particulate fraction (89 percent), most of the americium activity (97 percent) was associated with this fraction.

For ^{233}U and ^{234}U, total activities in the ground water sample were lower than in the surface waters. Despite the presence of significant quantities of particulates and colloids in each of the samples, over 99 percent of the total uranium activity was found in the dissolved phase, suggesting that uranium activity distribution is insensitive to particle concentration distribution in these waters. Analysis of fulvic acids isolated from the dissolved fraction showed that they are potentially important sorption substrates for uranium in these waters: in the ground water at well 1587, 14 percent of the total ^{233}U and ^{234}U activity was associated with the isolated fulvic acids. For the surface waters, 55 percent and 60 percent of the dissolved uranium activity was associated with the fulvic acid fraction at SW-51 and SW-53, respectively.

Particle Chemistry and Mineralogy

Preliminary assessment of particulate and colloid composition by chemical analysis of the isolates and by direct examination of particle concentrates by scanning electron microscope/energy dispersive x-ray revealed (1) relative consistency of composition of particles and colloids among the three sample sites, and (2) compositional differences between the particulates and colloids. Particulate composition of well 1587 ground water and SW-51 surface water was principally the inorganic elements silicon, iron, and aluminium; organic carbon was less than 10 percent by weight. SEM/EDX examination shows that the bulk of these particles were iron oxides, various layer silicates (including smectites, kaolinite, and micas), and silica particles. Iron oxides appeared to be a major part of the particulate fraction based on SEM/EDX and metal analysis. Particulates isolated from SW-53 were also predominantly composed of inorganic mineral species iron oxides and clay minerals, with calcite as a major constituent. The colloidal isolates at all three sites differed from the particulates in that organic carbon was a principal constituent, ranging from 55 percent of total analyzed colloid mass in the ground water at well 1587 to 95 percent of total analyzed colloid mass in the smallest colloid fraction at SW-51.

Summary

1. Colloidal-size particles (0.45 µm to 10,000 Daltons) comprised significant weight percentages of total particle mass in each of the waters examined. On a weight percent basis they were the predominant particle size range in two of the waters (well 1587 ground water and SW-51 surface water). Particulate-size particles (greater than 0.45 µm) comprised most of the particle mass at SW-53.
2. The isolated particulates appeared to be predominantly inorganic in composition, including iron oxides, layer silicates, and, at SW-53, calcite particles. Colloidal particles included the above minerals, but differed from the particulate composition in that organic carbon was a major constituent.
3. ^{239}Pu and ^{240}Pu activities in these waters were associated predominantly with the particulate fraction greater than 0.45 µ in size.
4. ^{241}Am activity distribution was more variable than the plutonium distribution among these sites. In the ground water sample, 73 percent of the total activity was associated with the dissolved and colloidal size fractions. In the surface water sample at SW-53, 97 percent of the total activity was associated with the particulate fraction.
5. More than 99 percent of the total ^{233}U and ^{234}U activities were associated with the dissolved fraction in these waters. Dissolved fulvic acids are a potentially important sorption substrate for uranium in these waters.

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MODEL VALIDATION AND DECISION MAKING—AN EXAMPLE USING THE TWIN LAKES TRACER TEST

By Natalie E. Olague, Paul A. Davis, Darrla Smith, *and* Tom Feeney

Introduction

Ground-water flow and transport model results are often used in making decisions concerning the safety of potential radioactive and hazardous waste disposal sites. Consequently, the validity of these results must be assured. There have been several international cooperative studies established [INTRACOIN (Swedish Nuclear Power Inspectorate, 1986), HYDROCOIN (Organisation for Economic Cooperation and Development, 1988), INTRAVAL (Andersson and Skagius, 1992), BIOMOVS (Swedish National Institute of Radiation Protection, 1990), and CHEMVAL (Read and Brody, 1991)] to address model validation with respect to the disposal of radioactive waste.

These studies have typically attempted model validation by comparison of model results with experimental data. Wherein, the objective of the modeling is to reproduce the experiment using all of the information available. However, in most cases (1) the experimental data are from experiments where all of the model input parameters have not been or cannot be measured independently of the experiment, and (2) the experimental results are available to the analysts before modeling the experiment. This leads to a calibration exercise and not a model validation exercise. In more recent validation studies, efforts have been focusing on predicting the results of experiments without knowledge of the experimental results to avoid potential biases. However, these experiments are still plagued by a lack of independent measurement of independent model parameters.

Regardless of the specific modeling approach adopted, the validity of the model is based on how well the model reproduces the experimental results. This conclusion is usually based on some measure of fitness or accuracy, either quantitative or qualitative, of some predefined performance measure. Therefore, the conclusion about the validity of the model is directly dependent on the performance measure chosen and degree of accuracy accepted. For example, one model may be able to predict moisture content at a certain location and time within 10 percent of the measured value, but cannot predict ground-water travel time within 50 percent. In addition, more complex models can always be derived to yield better and better fits with the data (usually based on calibration), and more than one model is usually able to explain the data. Consequently, these types of validation exercises become infinite and yield only ambiguous results.

Validation Approach

Our attempt to avoid these problems is to link the desired accuracy of the model results to the model use or purpose. This is consistent with Gass (1983) who states that the validity of a model depends on the real world aspect being analyzed. If this link is established, model validation becomes a process of building confidence that a model is acceptable for a specific purpose, and not the never-ending process of proving that a model reproduces reality.

With respect to the disposal of radioactive and hazardous wastes, the overall purpose of modeling is to aid in the decision-making process with regard to the safety of such disposal sites. Models are used to simulate quantities of interest (for example, dose, travel-time, concentration) related to safety that have been defined by the relevant expected site conditions and estimate the quantity of interest so that it can be used as an indicator for regulation. These quantities are usually estimated over relatively large spatial (meters, kilometers) and temporal (1,000 yr, 10,000 yr, 100,000 yr) scales, again, depending on the specific regulation. However, the purpose of modeling is not to precisely predict the quantity(s) of interest, which because of the large uncertainties associated with the time and spatial scales, cannot be done. Rather, the purpose is to simulate the expected site conditions and estimate the quantity of interest so that it can be used as an indicator of site safety and provide the basis for a decision. In light of this purpose, the seemingly insurmountable uncertainties associated with assessing the safety of a potential disposal site become manageable. In terms of this decision-making purpose, validation studies should provide a basis for making a confident decision about site safety. In fact, a model can be thought of as "valid" if it allows such a decision to be made and supported.

From a regulatory point of view, a model is acceptable as the basis for making a decision if it errs on the side of conservatism (that is, over-predicts the quantity of interest). More specifically, conservatism as the basis for a decision about safety is much more defensible than "realism" (since realism is undefinable). Therefore, the modeling approach that should be adopted for safety assessments is to start with simple and conservative models. If these model results indicate that the site can comply, then the regulator is comfortable licensing the site. If, on the other hand, these models indicate that the site cannot comply with the relevant safety standards, then the conservativeness can be decreased if there is a defensible basis to do so (for example, new site characterization data). Given the significance of conservatism in safety assessments, the basis for claiming that an analysis is conservative must be intently scrutinized. Validation studies thus serve the purpose of testing the conservatism of alternative models.

The specific information needed from model validation studies is the relative conservativeness of different modeling approaches compared to experimental data. This knowledge will in turn provide the basis to judge the adequacy of models used in support of safety assessments. For example, assume that a validation study indicates that one-dimensional flow and transport models consistently and significantly over predict the maximum concentration observed in a sandy aquifer tracer test. If similar one-dimensional models are used in support of a safety assessment at a similar site, the decision-maker has a basis for assuming that the model results are conservative. On the other hand, if it has been demonstrated that a model has consistently under predicted concentrations compared to experimental data, the decision-maker would be leery of accepting a safety assessment that used this model, without additional site characterization data.

Modeling Approach

Consistent with the above discussion, the modeling approach taken for this validation study consists of starting with a simple ground-water flow and transport model and then increasing model complexity (which typically results in decreasing model conservatism), the aim being to assess the relative conservatism of each model. The different models applied are developed by (1) making different assumptions about the type and nature of processes, (2) making different assumptions about existing data, (3) making different assumptions about the existence of data, and (4) different treatments of model parameter uncertainties. The results of these different modeling approaches are all compared to experimental data and are discussed with regard to the likelihood of making a defensible decision about safety.

As this work is sponsored by the U.S. Nuclear Regulatory Commission (NRC) Low-Level Radioactive Waste (LLW) Disposal Program, the specific purpose of this validation study is to provide the NRC staff with the basis to make a decision about the safety of potential low-level radioactive waste sites. The applicable regulation is 10 CFR 61 (U.S. Code of Federal Regulations, 1982) which limits the maximum annual dose to man after the site is closed. Therefore, to ensure consistency with the regulatory purpose, the performance measure for the comparison should be as close to dose as possible.

The experimental data base used in this validation study is the Twin Lakes 1983 Tracer Test conducted at Chalk River National Laboratory, Canada. The 1983 Twin Lakes Tracer Test is described in detail by Killey and Moltyaner (1988). In summary, the experiment consisted of a pulse injection of ^{131}I into a fully penetrating well. The tracer was then monitored for 45 days by downhole gamma counting in a set of dry access pipes. The access pipes are located on a grid approximately 40 m x 11 m with spacings of 5 m and 1 m, respectively. The geologic system consists of eolian sands overlying fluvially deposited sands. These sands are separated by a thin layer of garnetiferous sand and all of the sands lie on bedrock. The hydrologic system consists of a phreatic aquifer with the Twin Lakes located 40 m up gradient and a stream which serves as a ground-water discharge located 250 m down gradient. The Twin Lakes drain by recharging the underlying sand aquifer.

Results from three models were compared to the experimental data. Following the approach outlined above, simple models were applied first, followed by application of more complicated models.

Conclusions

The approach to validation proposed herein attempts to interpret modeling results in light of their intended use or purpose. That is, instead of attempting to find the "best" fit model to the experimental data, we attempt to determine the conservativeness or bias invoked by applying different models to simulate the same experiment. In this way we are able to provide guidance to the regulatory community on where they should expect model results to fall relative to actual data, and provide some assurance that certain model approaches consistently lead to conservative (that is, over estimates of concentrations and therefore dose) results and other modeling approaches lead to non-conservative results. Following this framework, we applied a series of models to the Twin Lakes Tracer Test. Simple (potentially conservative) models were applied first followed by the application of more complex (and perhaps less conservative) models.

Using complete ranges of available data and interpreting this data in several different ways, a simple conservative one-dimensional flow and one-dimensional dispersion model over-predicts the maximum concentration at a fixed location relative to the maximum concentration observed at the same location for the Twin Lakes 1983 Tracer Test. This builds some confidence that for a similar site these types of analyses would also be conservative. To extrapolate to the decision-making process, if a decision-maker were to accept a similar site based on these types of model results, there would be a relatively low chance that an unsafe site would be accepted. On the other hand, if the decision-maker were to reject a similar site based on these types of results there would be a relatively large chance that a safe site could be rejected (that is, the model may be "overly" conservative).

All of the models were conservative with respect to the tracer test when the laboratory-scale dispersivities were used. However, when the model-scale dispersivities were input only the one-dimensional model results were conservative. To extrapolate to the decision-making process, if the decision-maker were to accept a similar site based on multi-dimensional flow and transport model results using model-scale dispersivities there would be a relatively high likelihood that an unsafe site could be accepted. However, if a decision-maker accepts a similar site based on multi-dimensional model results using laboratory-scale dispersivities there would be a relatively low chance that an unsafe site would be accepted.

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A PERSPECTIVE ON GROUND-WATER MODELING FOR PERFORMANCE ASSESSMENT

By Clifford I. Voss

In 1891, Lord Kelvin gave what may be considered a motivation for much of the ground-water modeling done today:

> *In physical science a first essential step in the direction of learning any subject is to find principles of numerical reckoning and practical methods for measuring some quality connected with it. I often say that when you can measure what you are speaking about and express it in numbers you know something about it: but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind: it may be the beginning of knowledge, but you have scarcely, in your thoughts, advanced to the stage of <u>science</u> whatever the matter maybe.*
>
> *Lord Kelvin*
> *(Thomson, 1891, p. 80-81)*

A pioneer in the quantitative description of subsurface fluid behavior, M. King Hubbert, responded to Kelvin in a 1974 essay called, "Is being quantitative sufficient?" as follows:

> **** the Kelvin dictum equating the reliability of scientific knowledge with the extent to which quantitative methods have been employed may be a somewhat imperfect formulation, and one which in practice may lead to a considerable amount of misdirected effort. For, from what we have seen, some of the most profound results in the history of science have been obtained in geology by means of rigorous but essentially nonquantitative methods of analysis. We have also seen that whereas the employment of elaborate mathematical methods to quantitative data may produce valid results, they equally well may produce results which are fundamentally erroneous and in many situations highly misleading *** a blind adherence to the use of quantitative methods in geology can lead to results which are just as colossally erroneous or just as trivial as may be obtained by any other method.*
>
> *M. King Hubbert*
> *(Hubbert, 1974, p. 47)*

In the following, I present a perspective on ground-water modeling for performance assessment by considering the nature of a model, examples of model misuse and useful results, dealing with spatial variability and field data, the attributes of a good analyst, reducing the over-selling of modelling, and models in performance assessment. Although I focus my comments exclusively on the quantitative modelling of ground-water flow, a similar discussion applies to quantitative characterization of hydrogeological systems, whether it be in a hydrologic, geochemical, geophysical, geomechanical or other manner. Note that in discussion of these matters, I am relating the general sense of many colleagues at the U.S.Geological Survey (USGS).

Ground-water models are widely used today by government agencies, private industry and universities worldwide in attempts to solve problems of various types. The popular use of ground-water models results from the development of numerical methods over the past twenty years and the more recent accelerating growth in computing power. Whole technical conferences are dedicated to ground-water modeling. International groups meet regularly to discuss model validation for waste disposal problems. There is an international institute for ground-water modeling. We find model results admissible as evidence in court and use of models legislatively directed. Government regulators require numerical models and model predictions on a regular basis. Clients of consulting services have come to expect numerical modeling to be a part of the analysis they buy, and some projects are sold just on the basis of a modeling exercise. Numerous committees have been set up by technical organizations to evaluate existing models and to list code limitations. There are moves to regulate model use and to certify hydrologists. While all of the activity surrounding ground-water models is certainly laudatory to the pioneers of numerical modeling in subsurface hydrology, the rush to apply such technology to more problems by more people overshadows serious questions concerning the fundamental utility of the approach in many of these applications. Logical fallacies in analysis due to misapplication of model technology are widespread.

Basically, a ground-water model is a simple calculation stating only: "in a given volume of porous material, the amount of fluid mass that flows in less the amount of fluid mass that flows out gives the change in fluid mass in the volume." While this algorithm, called a fluid balance, is intuitively obvious, it is the major physical law involved in a ground-water model. Use of a computer to run a ground-water model only allows the volume for which we wish to calculate a fluid balance to have complex geometry and to be divided into many parts, and the simple mass balance calculation is applied individually to each part. Using a computer may allow calculation of a million of these small balances at once, but this does not change the basic physical meaning of the fluid balance calculation in a ground-water model, which is indisputably simple.

Difficulties arise when applying groundwater models to field problems. The fluid flows represented by models in calculating a fluid balance cannot be directly measured in the field except occasionally at wells and springs. Generally, only fluid pressures can be measured, and these only at specific points. Should a model need to be applied to a field problem and the model results checked for accuracy, a translation is required between the field-measured pressures and field flows. The translation typically used in groundwater models, Darcy's Law, has been determined experimentally, and requires measurement of pressure difference between two points and of the "ease of flow" between the points in order to determine the quantity of flow between the points. "Ease of flow" is generally referred to as permeability, hydraulic conductivity or transmissivity of the porous volume in question. The use of Darcy's Law introduces another difficulty, as pressures can be measured directly in the field, while "ease of flow" cannot.

In order to use a ground-water model to calculate the fluid balance in a particular field area, water pressures (or hydraulic heads) need to be measured and two further questions must be answered. (1) How much water flows in and out of the sides of the entire volume being modelled? This question is most often not considered carefully, and very rough estimates of flows at model boundaries are used. (2) What is the "ease of flow" in each of the small parts into which the entire volume has been divided for the sake of computer calculations? This second question is the focus of much current research in subsurface hydrology, and has no easy answer as hydrogeologic systems can have a complex structure and considerable variability.

The fact that a ground-water model is really only a simple device, and one which is difficult to employ in practice, is often obscured by the manner in which it is applied. The uninitiated model user and even many experienced model users believe that the numerical model can be made to give an accurate representation of field reality if only enough detail and data is included. At the USGS, we have seen modeling efforts in which field areas are divided into thousands of sub-volumes for the numerical model and a different value of ground-water recharge, transmissivity, and water withdrawal rate assigned to each of the volumes. These values are chosen in time-consuming manual work by attempting to match model calculated pressures with those obtained at measurement points in the field. This approach always results in a realistic-looking model in which parameter distributions appear complex. With modern computer-graphic rendering, such a model can be quite impressive to the uninitiated. In the final analysis, however, such a complex and expensive model usually reproduces field reality and makes predictions no better than a simple-looking model with fewer but larger subvolumes and the same constant value of recharge and transmissivity in each sub-volume. Because of the simple physical notion upon which the ground-water model is based, both the complex and simple model can calculate the total water balance in the entire volume with equivalent accuracy. The additional local variability which, by implication, is represented by the complex model, depends on the unknown spatial distribution of "ease of flow" and cannot, in fact, be represented with certainty.

Another example of a complex model that gives no better result than a simple model may be one with a clearly detailed representation of a known structure. For example, we have seen a cross-sectional representation of a landfill with various liners and covers. A very refined division of the landfill into subvolumes by the model user and careful assignment of flow at boundaries and "ease of flow" through each sub-volume resulted in a ground-water model that implied the certainty of a sophisticated standard engineering analysis. In reality, the flow through the landfill may be very sensitive to the "ease of flow" values of each layer and depend only on the vertical structure of these layers at any point. While the structure was indeed represented exactly in the model, the hydraulic properties of the layers were only estimated from laboratory analyses on similar materials. Here the real questions revolved not about the fine details of the structure of the modeled layers, as a layman would guess from pictures of the model in a report, but about the uncertainty in layer parameter values. A simpler one-dimensional vertical model would describe the same system, and focus analysis on the appropriate questions. It is not unusual that the ground-water model user with a complex model has so many details to deal with that the basic questions that ought to be identified by the analysis are not ever considered.

Another logical problem in model use is the one encountered by the analyst who is forced to create a model to solve a particular problem. At the USGS, we often receive calls from consultants and agencies requesting help with a ground-water model application. In many cases, the question to be answered is not even suitable for analysis by numerical modeling. However, it nearly always turns out that the model must be created to fulfill contractual obligations. So the analyst tries to find a way of using a ground-water model to answer a question which can really be answered only by other means or maybe cannot be answered at all. It is difficult for us to give good advice on how to best carry out a pointless exercise.

Consider, a last example, a problem of well contamination which has recently come to our attention. A briny waste disposal pond in a thin unconfined aquifer is underlain by a semi-confining unit below which is another aquifer containing water production wells which are downstream of the pond. Little data are available besides general stratigraphy and estimates of bulk hydraulic conductivity of the layers. The question that was posed by the contract for this work is, "How much waste will reach the wells in the lower aquifer?" with the requirement that the answer be determined using a ground-water model. A scoping analysis may indicate that, even though the pressure is lower at the wells than in the pond, the semiconfining layer will isolate the lower aquifer from contamination because of its low conductivity. In fact, diffusion of contaminant through the layer should be even faster than flow. After a long time when the contaminant finally diffuses through the layer, the lateral flow in the lower aquifer is so great that the diffusing contaminant is diluted far below levels of concern before reaching wells. All of this would become apparent from basic hand calculations, should the analyst have done them, and the results would eliminate any logical need for simulation except to make pictures. But what happens if there is a break or fracture in the confining layer or if old wells penetrating both aquifers have leaky corroded casings? This further question may appear to be a candidate for modeling analysis, especially considering that the contaminant is in a highly dense fluid that would tend to sink through an opening. The nature of the opening and "ease of flow" through it are unknown in this case, as no openings have been found at the site. Here again, the ground-water model analysis required by the contract has little value. The model can be made to allow any amount of contaminant to migrate through an opening depending on how the analyst describes it. For this study, the analyst needed to spend the bulk of effort just running the model, while the real hydrogeologic question on the structure of the confining layer and the possibility of cross-flow in old wells was overlooked. Requiring the best answer to the question of contamination, and not requiring a ground-water model analysis, would have been more effective for the clients in this case.

What are the results of a quantitative hydrogeologic analysis properly done, given that a ground-water model is used only if needed? First, the fundamental result of an analysis, what was learned, can usually be stated in a few sentences. The results include a list of factors controlling the system studied, the relationships among these factors, the sensitivity of system behavior to parameter values given in ranges, and interaction of the ranges. The results include alternative explanations of the same phenomena observed in data, or alternative behaviors that would be possible given the underlying controlling processes. The alternative behaviors may be called predictions by some. A properly done analysis clearly separates things known about the system from things that are still undefined or unknown. However, stating that any particular model used for the analysis is validated in any sense gives a false sense of confidence to those who will apply the results of the analysis.

As mentioned earlier, ground-water models allow the possibility of considering highly complex distributions of "ease of flow" parameters throughout the modelled volume. The most important recent advances in hydrogeologic modeling deal with either determining such distributions from sparse field data, or determining the characteristics of ground-water flow to expect in the field, given various hypothetical classes of complex parameter distributions. Determining spatial distributions from sparse field data is the goal of inverse modeling, parameter estimation, model discrimination, and statistical fitting techniques. The distributions resulting from such analyses are most often used directly in a ground-water model. Distributions are usually based on a simple geometric structure of regions, each containing relatively constant properties and on assumptions of smoothness in the spatial distribution. Because of this simplicity, their applicability is limited. On the other hand, these techniques do automate the calibration process and significantly ease the chore of creating a model for a particular site.

Determining the flow behavior that results from complex distributions is a major goal of stochastic hydrology. These analyses are based on assumptions of the statistical structure of "ease of flow" parameters in space, and do not predict a single spatial distribution but a multitude of distributions which fit the statistics and sometimes the field data as well. Used in a ground-water model, these distributions give a range of possible simulated behaviors as an outcome, with a probability assigned to each outcome. Stochastic methods would almost solve the problem of ground-water modeling in the face of sparse data were it not for the following fact. To determine the underlying statistical structure of the field volume in question for a stochastic model, requires even more data than a single simple model description of the system. Also, the statistical structure may not be constant over the field area, much as values of single parameters are not. But because of the lack of detailed data, stochastic methods usually assume a constant statistical distribution for a site. This may be as crude an approximation as the simple smooth spatial distribution assumed by fitting methods. On the other hand, theoretical analysis of various types of spatial variability may give needed insights into modes of behavior that would not be expected intuitively. To summarize, while the new modeling approaches have utility, neither the inverse nor stochastic approaches to ground-water modeling of a particular site lends additional certainty to quantitative predictions from modeling. Further, these may not effectively characterize the uncertainty in predictions.

There is a widely held view among model users and purchasers of model services that because models are a sophisticated technology involving computers, because as much data as exists for a problem can be included in a model, and because the model represents the physics of subsurface flow, that simulation of a particular problem or field site will inherently show ground truth. This view holds that the model itself is the vehicle of understanding and creation of a site model is the main object of work. The initiated know that nothing is further from the truth. Transferable knowledge is in the report, not in the numerical model. The report describes all of the considerations that went into the analysis and hypothesis testing leading to final form of the model. The real goal of work is the analysis. Thus the most important aspect of modeling is not which model to use, not the sophistication of the model's numerics, not the creation of realistic-looking simulated distributions, but the analysis. The ground-water model is simply the tool of the analyst much as a pocket calculator is a common aid to most of us. Although numerically correct, calculations with both are useless if not applied in a meaningful way to solve problems.

A meaningful analysis requires a good analyst. It is unfair to generalize about types of analysts, but I do it here to make a point. Clever, insightful application of ground-water models requires a healthy attitude. Those specialized in field techniques are generally concerned with small-scale phenomena and may not have the distance from the data to model insightfully. Those who exclusively run numerical models may use existing field data blindly and literally. Their task is most often only to get models to give results rather than to define and answer basic questions about a field area. However, those who deal with field data collection and data interpretation, as well as numerical models have the potential to develop a healthy attitude. These analysts know the futility of making a model too complex, and yet have detailed understanding of data and access to circumstantial information, never recorded, resulting from hands-on fieldwork, that leads to insights regarding the functioning of a ground-water system. The analyst with the benefit of combined field and modeling experience, is best equipped to make the expert judgements required to define and answer complex questions of performance assessment.

How can the overselling of ground-water models be reduced? Most buyers of modeling services don't know enough to do so, they keep buying. Consultants who would refuse lucrative, but pointless, contracts, would be bypassed by other consultants who are more willing to take on such modeling tasks. Universities dependent on model-development funds for research projects do not have a great interest in reducing overselling. Considerable responsibility rests with the USGS, as we, in the past, have pioneered and promoted ground-water modeling. Perhaps, some responsibility will be accepted by the Nuclear Regulatory Commission by demonstrating insightful analysis for performance assessment and by using models only in an appropriate manner. The view that the model itself is the object of a study will eventually disappear as clients requesting model analyses learn how little practical information they are gaining from many of these contracts. Requiring a model will again become less important than requiring hydrogeologic expertise.

What is the utility of ground-water models in performance assessment? It is possible that the most fundamental problem causing widespread misuse of models today is that the wrong questions are being posed to earth scientists concerning characterization and licensing of toxic and nuclear waste repositories, and clean-up of contaminated sites. Characterization and prediction of the fate of contaminants at sites are today required in an absolute sense. This is an impossible requirement considering the natural heterogeneity in the geologic environment which can never be described in detail and considering the uncertainty of climatic processes affecting a site. Expressing the probability of release levels from a repository for performance assessment is also not possible in a hydrogeologic system. It is not meaningful to express the uncertainty of measured field parameters, conceptual hydraulic models, scenarios and consequences in this way. The assignment of a likelihood for a given scenario is an even less certain procedure than making predictions from ground-water models. Understanding of what is going on is only further muddled by this. The compound probability of all assumptions required to determine whether a specific release consequence will occur thus has little practical meaning.

Absolute criteria for safe disposal are and will in the foreseeable future be impossible to guarantee from any program of site characterization and quantitative modeling conceivable. Existing legislation that specifically mandates such characterization and subsequent modeling does not necessarily result in the most effective public risk reduction that is possible today. A more meaningful approach may be to determine whether one disposal site is better than another site. Relative ranking of sites and isolation technologies, is a question that modern earth sciences can more realistically deal with. Performance assessment for underground disposal must be based on a consensus of expert judgement of long-term safety, and not on any calculated criterion. Quantitative performance assessment and modeling is valuable only if it can identify issues that must be considered when reaching such a consensus on relative ranking. Hopefully, the regulations will adapt as awareness grows concerning the significant uncertainty concerning uncertainty in hydrogeologic systems, and more realistic goals will instead be set.

Disposal of nuclear wastes is, in principle, an engineering project, but the performance assessment through its dependence on hydrogeology will always be more of an art requiring expert judgement. Ground-water models are only valuable for intuition building, not for quantitative prediction of consequences. As a result of critically exercising such models, skill can be developed in the "art" of performance assessment. With greater intuition, technically sound but simple analyses, (for example, analysis in one spatial dimension) can more authoritatively be selected with which to carry out performance assessment.

As M. King Hubbert did in his essay, "Is being quantitative sufficient?", this perspective on ground-water modeling for performance assessment will conclude with the thought of Maurice Biot, a pioneer in the quantitative description of mechanical deformation of porous media, on the analysis of complex problems:

> *Deeper physical insight combined with theoretical simplicity provides the short-cuts leading immediately to the core of extremely complex problems and to straightforward solutions. This cannot be achieved by methods which are sophisticated and ponderous even in simple cases.*
>
> *Maurice A. Biot*
> *(Biot, 1963, p. 89)*

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PRELIMINARY INVESTIGATIONS INTO THE ROLE OF ORGANIC COMPLEXANTS AND MICROPARTICULATES IN THE ENHANCEMENT OF RADIONUCLIDE TRANSPORT

By Alan J. Schilk *and* David E. Robertson

Introduction

A major concern regarding the operation of existing and projected nuclear waste disposal sites is the incidence of subterranean radionuclide transport by saturated and/or unsaturated flow. This phenomenon could potentially result in the contamination of public water supply systems as well as uptake by overlying vegetation, thereby directly or indirectly exposing the general public to such materials. Unfortunately, the physico-chemical processes that expedite such transport are still not well understood. To more fully comprehend the mechanisms that determine the extent of radionuclide migration or retardation in existing or proposed natural settings, it is imperative that those species exhibiting facilitated transport be examined in actual field situations and the results subsequently compared to predictions from laboratory and thermodynamic data. Fundamental information of this sort can then be incorporated into transport models for more accurate predictions of radionuclide migration from repositories, thereby enhancing strategies for site planning or remediation by facilitating mobilization (for pump-and-treat methodologies) or deposition (for ensuring retention).

To assist in the characterization of these processes, a preliminary study was initiated at Chalk River Laboratories (CRL) in Ontario, Canada, in an attempt to identify and quantify the mobile radionuclide species originating from three separate disposal sites: (1) the Chemical Pit, which has received aqueous wastes containing various radioisotopes, acids, alkalis, complexing agents, and salts since 1956; (2) the Reactor Pit, which has received low-level aqueous wastes from a reactor rod storage bay since 1956; and (3) the Waste Management Area "C," a 30-yr-old series of trenches containing contaminated solid wastes from CRL and various other facilities. These mature low-level waste management and experimental disposal sites are excellent analogues for shallow-burial facilities located in humid environments, and they provide a unique and invaluable opportunity to study the long-term behavior and transport of a number of important radionuclides, many of which have resided in this shallow groundwater flow system for nearly 40 yr.

It is the purpose of this paper to briefly discuss the experimental procedures utilized in this field study at CRL, and to present the preliminary data obtained as a result.

Site Description

The local geology at CRL is made up of a variety of unconsolidated Quaternary sediments of glacial, fluvial and aeolian origin overlying a topographically irregular and locally fractured bedrock of Precambrian granitic gneiss, typical of much of the Canadian Shield. The surficial deposits (generally less than 30 m in thickness) are fine to medium sands with interbedded layers of clayey silt, both of which are composed largely of quartz and aluminosilicate minerals with associated alteration products, and trace amounts of hydrated oxides of iron and manganese, sulfides, carbonates, and organic matter (Champ and others, 1985). Annual precipitation, approximately 75 cm, is distributed evenly throughout the year and recharges a water table normally less than 5 m from the ground surface. This has led to the formation of numerous swampy areas throughout the region, which contain bog deposits of peat and other organic matter.

The CRL Liquid Disposal Area incorporates a series of lined and unlined trenches excavated from surface sands and includes the Chemical and Reactor Pits (see figs. 10, 11). Low-level waste disposals to the former began in the mid-1950s and included a host of radionuclides, acids, alkalis, complexing agents, and salts that originated from various operations at the facility (Killey and Munch, 1984). According to Champ and others (1985), the total inventory of ^{60}Co on the aquifer matrix downgradient of the Chemical Pit is 370 GBq (gigabecquerels) (10 Ci), while the quantity of α-emitters disposed of at this site was estimated to be 185 GBq (5 Ci). A short subsurface flow path extends from this pit to a nearby stream, with a ground water residence time of 6 months to 2 yr and a mean flow of

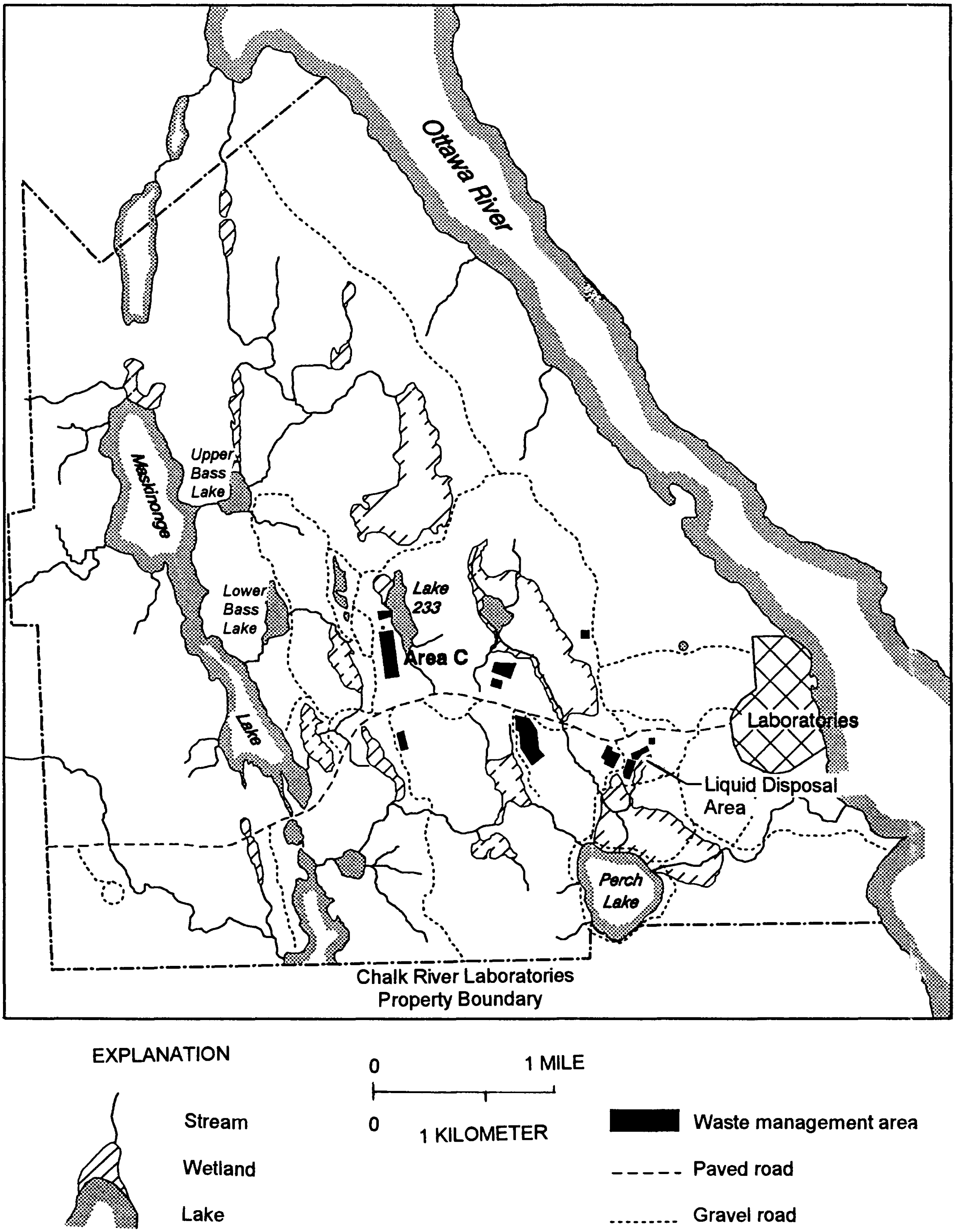

Figure 10. Location of Chalk River Laboratories and the waste management areas.

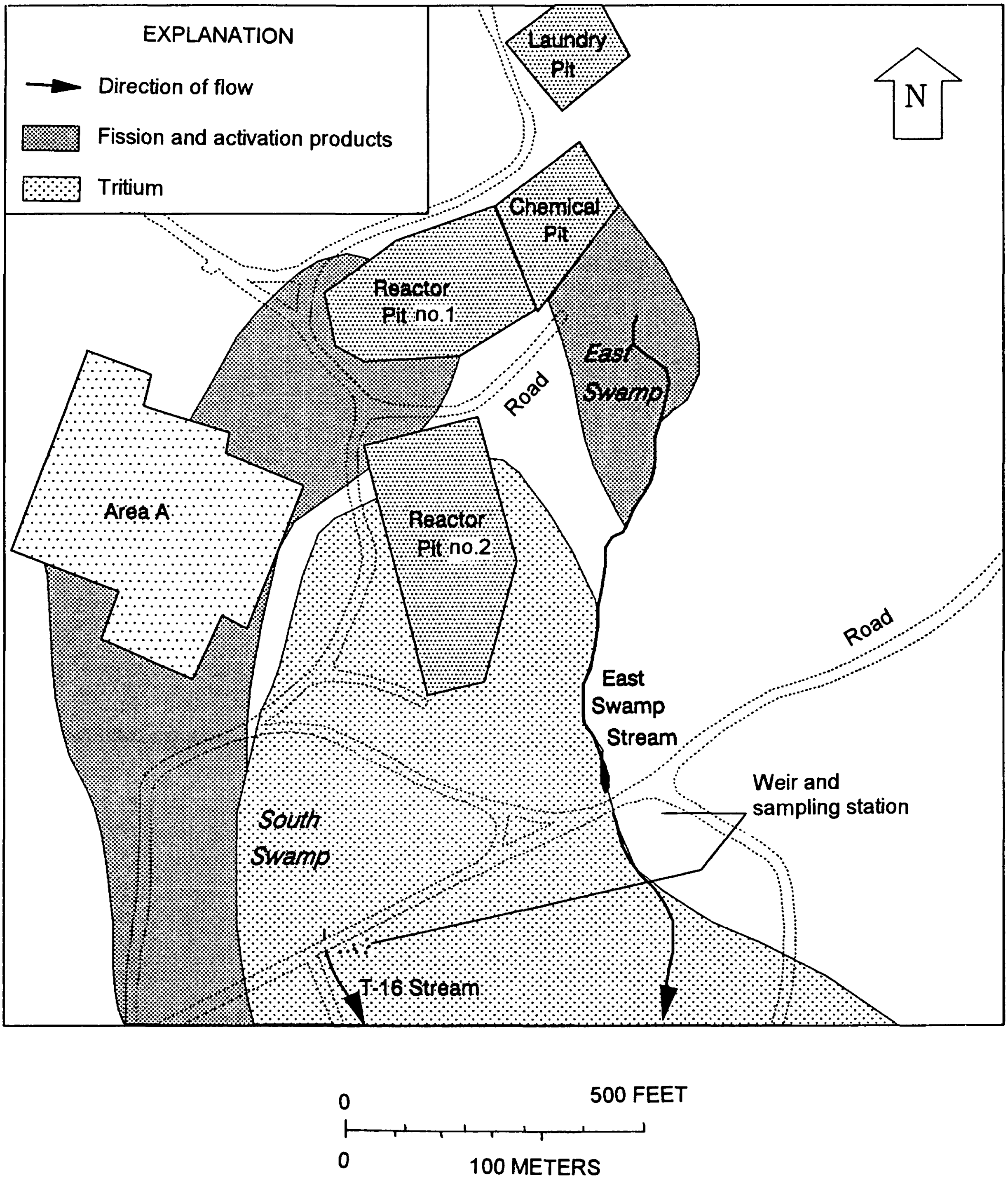

Figure 11. Subsurface plumes of tritium and fission and activation products from the liquid disposal area and waste disposal area A.

5 to 25 cm/day. Earlier investigations identified radioisotopes of Co, Zr, Ru, Sb, Cs, Ce, Eu, Fe, Sr, Ni, I, Tc, Pu, Am, and Cm in downgradient water samples. Nonetheless, routine monitoring of Perch Lake, which receives drainage from this waste pit, indicates that radionuclide concentrations do not exceed levels prescribed for permissible drinking water (Killey and others, 1984).

The Reactor Pit has received low-level aqueous wastes from CRL's rod storage bays since 1956. Disposed α-emitters total approximately 580 GBq (15.8 Ci), while groundwater flow and residence times are essentially equivalent to those observed at the Chemical Pit located 200 m to the northeast. Champ and others (1985) have determined the presence of radioactive Co, Ru, Sb, Cs, Fe, Sr, Ni, Pu, and Am in the ground-water effluent from this site.

Waste Management Area "C" includes a series of unlined trenches within a large sand ridge, which forms the southern margin of a nearby lake. This facility is still in operation and has received mixed low-level solid wastes from CRL, industry, hospitals, and universities throughout Canada since 1963. Water is discharged from the lake to the southwest via the potentially contaminated subsurface sands and travels at rates of 15 to 30 cm/d, leading to a total residence time of approximately 2 to 4 yr below Area "C" (R.W.D. Killey and J.F. Mattie, written commun., 1991). Tritium is the primary radionuclide of concern at this site in terms of quantity, although anomalously high concentrations of ^{14}C have been detected in the downgradient vegetation; ^{60}Co and ^{36}Cl have been observed in the ground water as well. Impermeable polyethylene covers were installed over a large portion of this site in 1983 and appear to have eliminated the infiltration of precipitation and consequent release of tritiated water, but ^{14}C is apparently still migrating from the area (R.W.D. Killey, oral commun., 1993).

Experimental

Ground waters were sampled at each of the above sites from existing multilevel piezometers, which were known from previous investigations to intercept the subsurface plumes of migrating radionuclides. Individual piezometers were flushed for about 30 minutes before collection to ensure representative sampling of interstitial waters, and pump flow rates were maintained as low as possible to preclude resuspension of any microparticulates retained by the aquifer medium. Following the flush procedure, samples were passed through a sterile prefilter unit, which included a nominal 1.0 µm gauze layer followed by 0.8 µm and 0.2 µm membranes in an attempt to retain a majority of the particulate, or undissolved, materials. During this process, groundwater temperature, pH and Eh, dissolved oxygen, alkalinity, and ferric/ferrous iron concentrations were quantified. Aliquots were also drawn for analyses of trace metals, anions and organic carbon content.

Prefiltered groundwaters were subsequently passed through a large-volume-water sampler (Robertson and Perkins, 1975) to facilitate the removal of charged and uncharged soluble species. This modular unit is composed of six stacked resin or powder chambers separated by glass-fiber filter sheets. Water enters the base of the unit and is directed to the first of two cation-exchange-resin beds (sodium [Na$^+$] form, 200-400 mesh), the redundant bed being present in case the first is compromised or becomes saturated. Following the cation beds are duplicate layers of anion-exchange resin (chloride [Cl$^-$] form, 200-400 mesh) for retention of negatively charged species, and two activated aluminum-oxide powder beds for the removal of those radionuclides that remained in soluble, non-ionic forms. The individual resin and powder beds (as well as the prefilter components) were carefully packaged and shipped to PNL for radiological characterization. Specifically, nondestructive gamma-ray spectrometry was performed by placing the filters, resins, and powders in standardized geometries and counting them with a lithium-drifted germanium detector. Aliquots of the above were then leached with appropriate reagents, and the resulting solutions were subjected to various radiochemical separation procedures for the quantification of radioisotopes that were not amenable to direct gamma analysis.

Results and Discussion

Ground-water samples from the Chemical Pit, Reactor Pit, and Waste Management Area "C" are observed to be slightly acidic and mildly or highly oxidizing in nature (see Schilk and others, 1992). The Eh, dissolved oxygen, and ferric/ferrous iron data indicate that the Chemical and Reactor Pits are nearly saturated in terms of oxygen content, while the "C" Area represents a considerably less oxidizing environment. Dissolved organic carbon concentrations at the Chemical and Reactor Pits appear to be typical of shallow, unconfined aquifers in humid regions, whereas that in Area "C" is somewhat lower. In addition, alkalinity results for the latter seem to indicate an elevated carbonate content at this site.

Sulfate and chloride are the primary anions in solution at these sites, while nitrate is prevalent at the Chemical Pit only. These results are reasonable when one considers that two of the primary geochemical inputs to this region are dissolved sodium chloride and acid precipitation (composed largely of sulfate, nitrate, and chloride). The third major input into the Chemical and Reactor Pits—namely, liquid radioactive waste disposals—probably contributed to the nitrate concentration in the former as a nitric acid component.

Trace element behavior appears to reflect the local geologic/mineralogic environment, most notably with regard to the abundance of the major rock-forming elements silicon, sodium, calcium, magnesium, and iron. The iron content in Area "C" waters is particularly elevated as, indeed, are most of the elements at this site with respect to those at the Liquid Disposal Area. The elevated iron concentration may be a function of the less oxidizing nature of the "C" Area groundwaters, which could have led to a predominance of the more soluble ferrous species. In any case, the above groundwater data are not significantly different from those reported by Champ and others (1985) for the Chemical and Reactor Pits, suggesting that, despite disposal practices that often varied both temporally and in actual content, these groundwaters are apparently quite stable in terms of their geochemical make-up.

Isotopes of cobalt, ruthenium, antimony, and plutonium are present in waters downgradient from the Reactor and Chemical Pits, while only cobalt could be accurately quantified near the "C" Area. It is readily apparent that anionic species predominate in each case, most often followed by nonionic, cationic, and particulate species in order of decreasing concentrations. It is suspected that the negatively charged species are primarily (1) organic macromolecules of natural humic and fulvic acids originating from the decomposition of plant and animal residues, and (2) anthropogenic organic chelating agents such as ethylenediamine tetra-acetic acid (EDTA), a number of which are known to have been disposed of within the Chemical Pit. Other potential forms of these migrating radionuclide-bearing anions may include inorganic colloidal materials mineralogically equivalent to the aquifer matrix, with negatively charged surface sites favorable for the retention of cationic radionuclides) and inorganic radionuclide complexes composed of common aquo-anion ligands (sulfato-, chloro-, hydroxo- [OH$^-$], etc., or combinations thereof).

The nature of the cationic species, on the other hand, is harder to predict since by virtue of their overall charge the aquifer medium would be expected to have retarded their migration and precluded their presence down-gradient from the source. Uncertainty exists at this time as to whether these cations are "original" species or were generated as a result of some denaturation phenomenon upon passage through the initial cation exchange bed.

The prefiltration results from this initial study seem to suggest that particle-size fractionation may serve to segregate individual species and allow further elucidation of their structure by other (for example, spectroscopic) means. As an example, one might expect that a majority of the microparticulate/colloidal radionuclide species would reside in the smallest fractions, since these would exhibit larger specific surface areas and, consequently, higher radionuclide retention capabilities per unit mass. Indeed, a great deal of recent and projected research has targeted a variety of organic (for example, humic and fulvic macromolecules) and inorganic microparticulate/colloidal materials, which are suspected of acting as vehicles for the facilitated transport of radionuclides and other contaminants of interest. If significant size/speciation diversity does exist in the smaller submicron range, then ultrafiltration would seem an appropriate means of separating individual migration species into "purer" fractions, thereby facilitating future detailed radionuclide speciation studies. Clearly, additional methodologies are needed to unequivocally identify the actual form(s) of these migrating species, although these initial resin-based studies have afforded some invaluable heuristic data.

Acknowledgments

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MODELING THE GEOCHEMICAL EVOLUTION OF GROUND WATERS IN THE CENTRAL OKLAHOMA AQUIFER, OKLAHOMA

By David L. Parkhurst

Introduction

The Central Oklahoma aquifer is a freshwater flow system in central Oklahoma that is unconfined in the eastern two-thirds, but is confined in the western one-third of its extent. The geologic units of the aquifer are interbedded sandstones and mudstones. Quartz and clay minerals are the major detrital constituents; authigenic dolomite, calcite, and kaolinite are present. In general, the aquifer contains calcium-magnesium bicarbonate water in the unconfined part and sodium bicarbonate water in the confined part. Sodium chloride water is found below freshwater throughout central Oklahoma. Analysis of the chemical and petrographic data and geochemical modeling have identified the predominant geochemical reactions that control the ground-water compositions to be (1) uptake of carbon dioxide, (2) dissolution of dolomite and to a lesser extent calcite, (3) cation exchange of calcium and magnesium onto clay minerals with the release of sodium, and (4) mixing of freshwater with preexisting brines (Parkhurst, Christenson, and Breit, 1993). These reactions cause the formation of several geochemical fronts which migrate through the aquifer, including the (1) transition from brine to fresh water, (2) transition from sodium- to calcium- and magnesium-rich clays, and (3) depletion of calcite and dolomite. The computer code PHREEQM was used to model the geochemical reactions in the aquifer and to estimate the rates at which the geochemical fronts migrate. To illustrate applications of the code to ground-water transport of radionuclides, the program was used to model the migration of a pulse of radium, which hypothetically was introduced as a contaminant at the surface of the aquifer.

Processes

In the unsaturated zone of the Central Oklahoma aquifer, recharge water takes up carbon dioxide that is generated by the respiration of plants. Partial pressures of carbon dioxide (0.1 to 0.01 atmospheres in recently recharged water) and carbon-13 isotope ratios (-10 to -20 permil, relative to Peedee Belemnite) in water samples indicate an unsaturated-zone, plant-derived source of carbon dioxide. As a result of the uptake of carbon dioxide by recharge, dolomite and calcite dissolve, either within the unsaturated or within the saturated zone. Three lines of evidence suggest that dolomite is the primary carbonate reactant: (1) The abundance of dolomite (1 to 7 weight percent) is much greater than that of calcite (generally less than 1 percent or undetectable); (2) calcium and magnesium are present in equimolar concentrations in ground water; and (3) exchangeable calcium and magnesium in clays are present in approximately equimolar concentrations. The combination of uptake of carbon dioxide by recharge water and dissolution of dolomite produces waters in which calcium and magnesium are the predominant cations, and bicarbonate is the predominant anion.

This calcium-magnesium bicarbonate water composition is present almost exclusively in the unconfined part of the aquifer. In many parts of the shallow, unconfined aquifer, water is undersaturated with dolomite and calcite. In these locations, lack of carbonate minerals seems to limit the amount of carbonate mineral dissolution. In all other parts of the aquifer, water is saturated with dolomite and calcite which indicates carbonate minerals are dissolving in sufficient quantities to produce equilibrium.

Apart from the uptake of carbon dioxide and the dissolution of dolomite, the most important reaction in the freshwater flow system is cation exchange on clays. Where calcium-magnesium bicarbonate water exists in the unconfined part of the aquifer, sodium concentrations in the water are small. Here, clays contain a small fraction of exchangeable sodium, frequently less than 1 percent of the exchangeable cations. By contrast, in the confined part of the aquifer and in the clay-rich parts of the unconfined aquifer, sodium concentrations in the water are large and calcium and magnesium concentrations are small. In these parts of the aquifer, the clays contain a large fraction of exchangeable sodium, up to 50 percent of the exchangeable cations. The transition in water compositions from small to large sodium concentrations is explained by an exchange of calcium and magnesium onto the clays with the release of sodium to the water. The cation-exchange reaction causes a small amount of dolomite to dissolve to maintain dolomite equilibrium. However, the primary effect of the dissolution is to raise the pH to the range 8.5 to 9.1 with only a small increase in the bicarbonate concentration.

One other process that is important to the major-element chemistry of the Central Oklahoma aquifer is the mixing of freshwater with sodium chloride brines. Brines underlie the freshwater throughout the study unit and it is reasonable to assume that in the geological past, brines filled all of the geologic units. The brines have persisted for tens of millions of years below the aquifer, so it is evident that these brines are moving very slowly if at all. Similar bromide to chloride ratios between the brines underlying the aquifer and the water within the aquifer indicate that the brines are the source of chloride in the freshwater.

Modeling

Reaction-transport modeling using the program PHREEQM (Appelo and Willemsen, 1987; Appelo and others, 1990; Appelo and Postma, in press) provides a plausible synthesis of the chemical analyses of brines and freshwater and the petrographic and cation exchange data. The program is capable of modeling the simultaneous processes of advection, dispersion, and chemical reactions. The conceptual model for the program is very intuitive. The program considers a set of cells arranged in one dimension. Advection is accomplished by transferring the water in one cell to the adjacent cell in the downstream direction, referred to as a "shift" in the program documentation. Dispersion is represented by mixing the waters in adjacent cells. To simulate large dispersivities, mixing of adjacent cells may be performed more than once for each shift. After each dispersive mixing step or advective shift, the water within a cell is equilibrated with the cation exchanger present in the cell and with any minerals that are stipulated to be in equilibrium. Thus, PHREEQM models advective and dispersive transport assuming exchange equilibrium and mineral equilibrium within each cell at all times. Although PHREEQM does not explicitly solve the advective-dispersive partial differential equations of solute transport, it calculates results that are in excellent agreement with analytical solutions to these equations (Glynn, Engesgaard, and Kipp, 1991).

The modeling with PHREEQM assumed the aquifer initially was filled with a brine composition typical of the most concentrated brine analyses from the units underlying the aquifer. Rainwater, evaporated twenty fold (as estimated from rainfall minus runoff divided by ground-water discharge) and equilibrated with atmospheric carbon dioxide, was assumed to enter the aquifer and gradually displace the brines by advection and dispersion. Based on point counts of thin sections of aquifer material, dolomite and calcite were estimated to be present at concentrations equal to 5 percent and 1 percent of the rock volume. These minerals were assumed to equilibrate instantaneously with water as long as they were present. The clays in the aquifer initially were in exchange equilibrium with the sodium, calcium, and magnesium concentrations in the brines and remained in equilibrium with the freshwater as it invaded the aquifer. A soil zone was simulated by assuming the first cell in the model was open to carbon dioxide and the partial pressure of carbon dioxide in that cell was fixed at $10^{-1.5}$ atmospheres.

The migration of radium through the aquifer due to hypothetical contamination of the water and clays in the surficial aquifer was modeled by introduction of elevated radium concentrations to the first cell of the model at the beginning of the simulation. At time zero, the concentration (relative to a kilogram of water) of radium on the exchanger in the first cell was 3.9×10^{-4} mol/kg water (moles per kilogram water), which resulted from equilibrium with a specified dissolved radium concentration of 10×10^{-6} mol/kg water. In all other cells at time zero, the concentration of radium on the exchanger was 1.1×10^{-7} mol/kg water, which resulted from equilibrium with a specified dissolved radium concentration of 1×10^{-10} mol/kg water. Radioactive decay of radium was not considered in the simulation.

The exchange constants for calcium and magnesium, relative to sodium, were fit to clay cation exchange data for 18 core samples from the Central Oklahoma aquifer. The mass-action equation used had the following form:

$$K_{ex} = \left(\frac{[Me_{0.5}X]}{[NaX]}\right)^{n} \frac{[Na^{+}]}{\sqrt{[Me^{2+}]}} \qquad (1)$$

where K_{ex} is the equilibrium constant, Me represents either calcium or magnesium, X represents an exchange site, brackets indicate activity, and *n* is a fitting parameter derived from regular solution theory (Garrels and Christ, 1965, p. 268-276). A value of *n* equal to 0.65 was used for calcium, magnesium, and radium in all calculations. The fit values for log K_{ex} for calcium and magnesium are 0.64 and 0.52 (table 6). Radium was assumed to be similar in chemistry to barium and was given a larger log K_{ex} (0.94), indicating a greater affinity for exchange sites in the clay than the other cations. An ionic strength dependence was given to each equilibrium constant: log K_{ex} = log K_{ex} + bI. The *b* parameter effectively varied the fraction of sodium on the exchange sites at initial conditions, when brine filled the flow tube. A value of *b* equal to 0.05 produced an exchanger with about 45 percent exchangeable sodium, which was approximately the largest percentage of exchangeable sodium determined in any core sample. A listing of the input data for PHREEQM is given in table 6.

Table 6. Parameters for PHREEQM
[mol/kg water, moles per kilogram water]

Parameter	Run
Number of cells	20
Cell length, meters	2.5
Dispersivity, meters	0.1
Time step, years	1.0
Velocity, meters per year	2.5
Length of simulation, years	10,000
Porosity	0.2
log K Ca-Na exchange	0.64
log K Mg-Na exchange	0.52
log K Ra-Na exchange	0.94
Exchanger, mol/kg water	0.4
Calcite, mol/kg water	1.0
Dolomite, mol/kg water	2.7
P(CO_2) of first cell, atmospheres	$10^{-1.5}$

Results

The results of the model are consistent with the conceptual model for geochemical evolution of ground water in the study unit. At a given cell within the model (fig. 12 plots model results for cell 4, 7.5 to 10 m down the flow tube), the water composition evolves with time from a sodium chloride brine (0 to 4 yr, fig. 13), to a sodium bicarbonate water (4 to 50 yr), and finally to a calcium magnesium bicarbonate water (after 50 yr) as freshwater displaces brines. At the same time, the modeled composition of the clay evolves from a sodium-rich clay to a sodium-poor clay. The radium pulse reaches a maximum concentration in cell 4 at about 200 yr, after which radium concentrations continuously decrease. At approximately 2,000 yr, the dolomite and calcite have been removed from the first cell, and an increase in pH and decreases in dissolved calcium and radium propagate through the flow tube. The pH increases because the water no longer equilibrates with carbonate minerals at a fixed P(CO_2) of $10^{-1.5}$. The water entering the flow tube still has a P(CO_2)of $10^{-1.5}$, but equilibration with carbonates occurs in a cell that is closed to carbon dioxide gas. The result is that the P(CO_2) in equilibrium with the carbonate minerals is less than $10^{-1.5}$ and the pH of the water is greater. The dissolved concentrations of calcium and radium decrease in response to the increased pH.

The results of the model also are consistent with the chemical analyses of groundwater and brines in central Oklahoma. The modeling results are plotted on figure 13 along with all data from the current study of the Central Oklahoma aquifer and all brine data from geologic units underlying the aquifer. The brine is in the upper right of the diagram, with large concentrations of both calcium and sodium. The sodium bicarbonate water is at the nadir of the curve, where sodium concentrations are approximately 0.01 mol/kg water, but calcium concentrations are less than 0.0001 mol/kg water. As the sodium on the exchanger is exhausted, the water composition moves up the curve to the left edge of the diagram, where calcium concentrations are approximately 0.002 mol/kg water, but sodium concentrations are less than 0.001 mol/kg water. Most of the data from the study unit, both freshwater and brines, plot near the simulated reaction path.

The model results were used to estimate the rates at which several geochemical fronts would move through the aquifer for the specific conditions used in the model. First, the brine-freshwater interface moves approximately as fast as the flow velocity, 2.5 m/yr. Secondly, the interface between calcium-magnesium dominated water moves at approximately 0.15 m/yr. Thirdly, the migration of the maximum radium

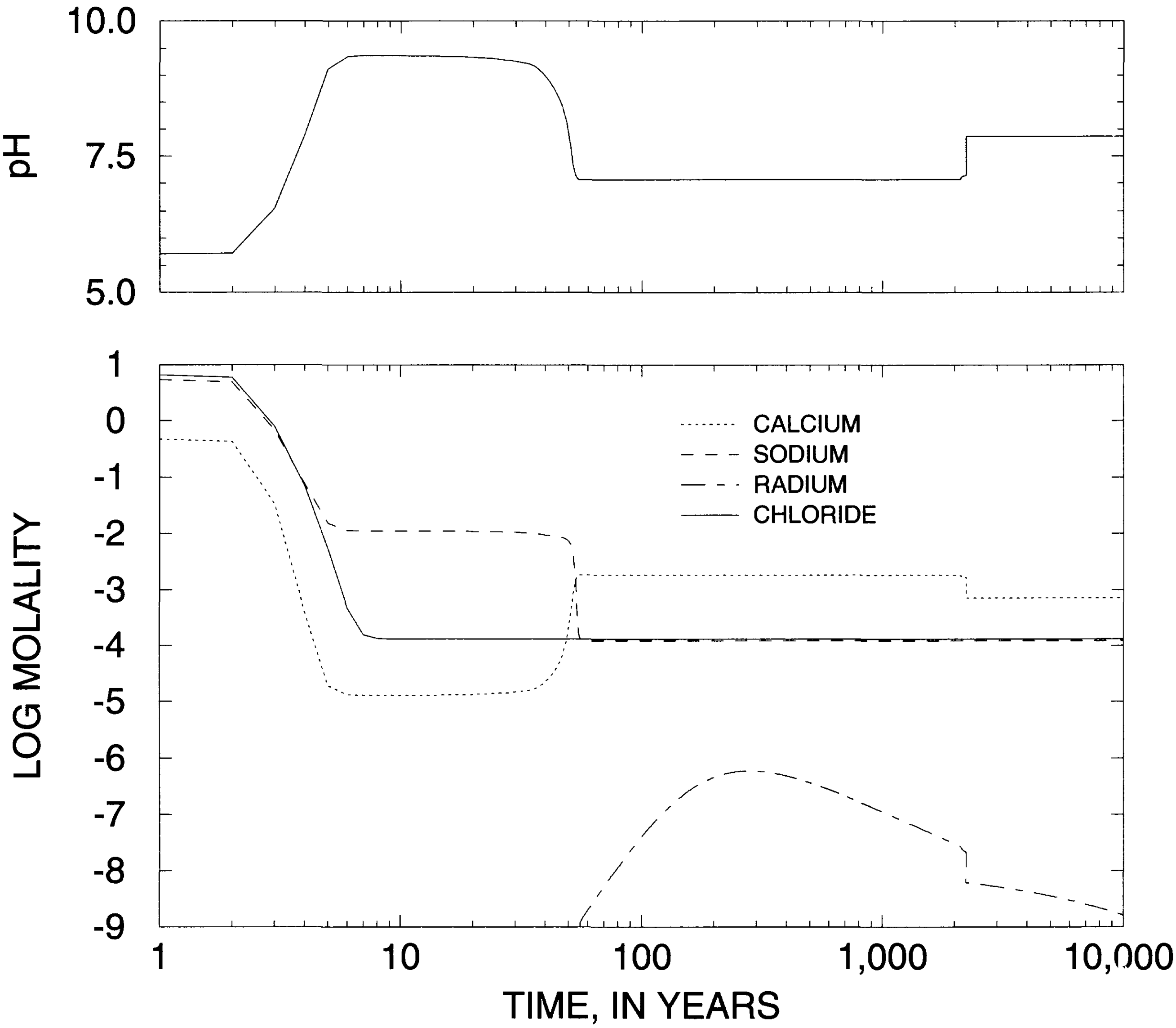

Figure 12. Chemical evolution of water in the Central Oklahoma aquifer as modeled by PHREEQM. Simulation results are for water in cell 4, 7.5 to 10. 0 meters into the flow tube.

concentration varies with time. Initially, the maximum concentration moves at approximately 0.035 m/yr. At the end of the simulation, the rate of migration is less than 0.005 m/yr. Finally, in the unsaturated zone, the removal of calcite and dolomite proceeds at approximately 0.001 m/yr. After calcite and dolomite are removed from the unsaturated zone, the removal of calcite and dolomite in the saturated zone proceeds at approximately 0.0004 m/yr.

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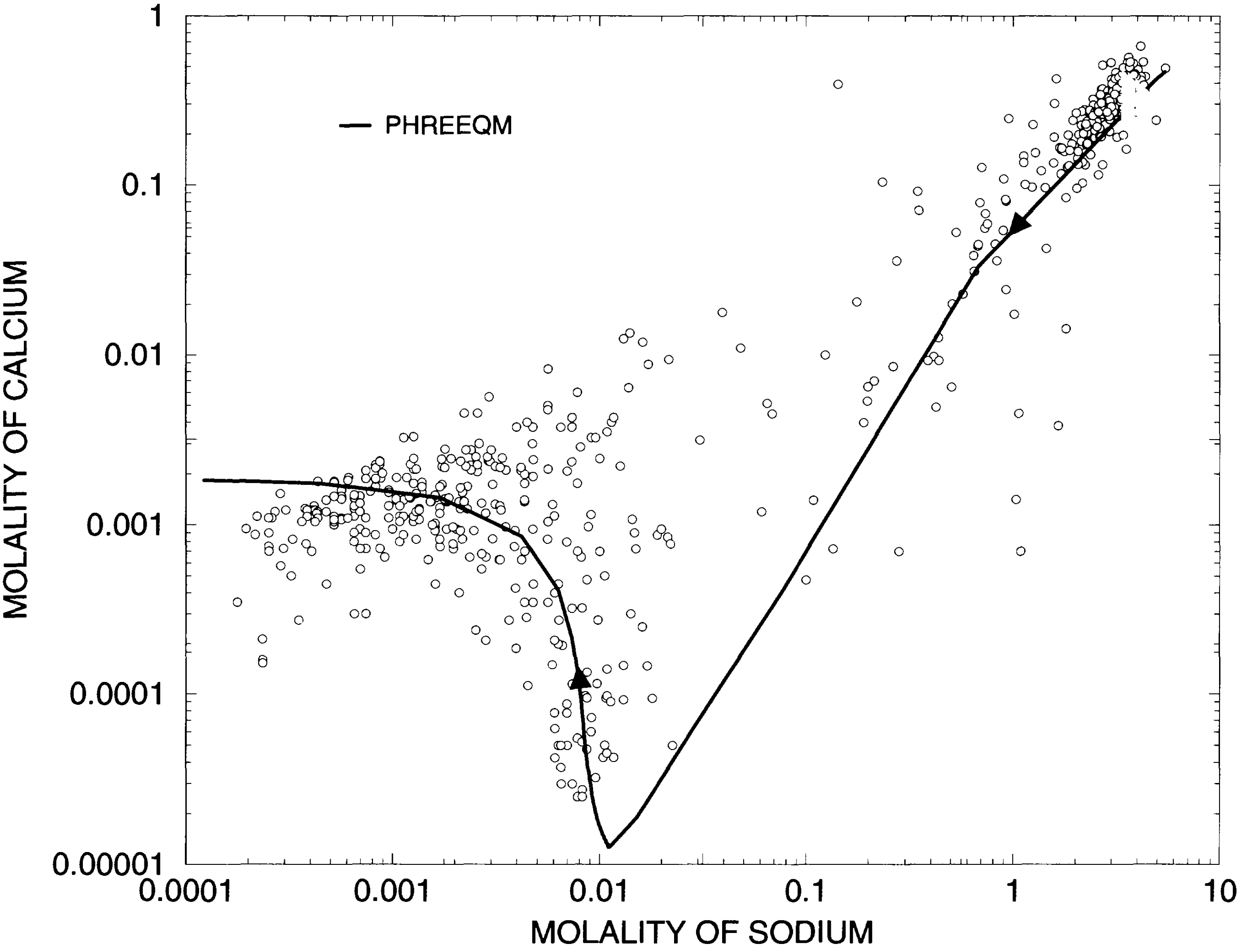

Figure 13. Comparison of PHREEQM simulation with data from the study unit, including data from brines underlying the Central Oklahoma aquifer. Arrows indicate the simulated direction of change in chemical composition with time.

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CHLOROFLUOROCARBONS (CFC'S) AS TRACERS AND AGE-DATING TOOLS FOR YOUNG GROUND WATER—SELECTED FIELD EXAMPLES

By L. Niel Plummer *and* Eurybiades Busenberg

Introduction

Ground-water traveltimes provide important information in the characterization of hydrologic environments at sites for storage of low-level nuclear wastes. Ground-water traveltimes are usually determined by numerical simulation of ground-water flow. Errors in the calculated flow velocities and traveltimes result from uncertainties in the areal rates of recharge, the boundary conditions, and the hydraulic properties of the aquifer. Ground-water age dating can provide independent information that can aid in the flow-model calibration process because the water age is influenced by the hydraulic properties of the sediment and rock along the flow line from the point of recharge to the sampling point. Comparison of modeled traveltimes and measured traveltimes at specific points in the flow system is an important approach to model calibration.

Applications of environmental tracers to hydrologic systems can provide independent definition of the time since a parcel of water was isolated from the atmosphere. With ground-water age-dating it becomes possible to (1) relate observations on the spatial distribution of substances in ground water to the actual time of introduction, and (2) refine flow models to improve their predictive capabilities in site-characterization studies. Plummer and others (1993) compare and contrast uses of environmental tracers in age-dating young ground water.

This paper presents applications of chlorofluorocarbon dating of ground water in two very different hydrologic environments. The CFC-dating method is first demonstrated for shallow water-table aquifers on the Delaware-Maryland-Virginia (Delmarva) Peninsula of the Atlantic Coastal Plain. CFC's are then used to investigate recharge mechanisms and traveltimes in ground water from the Snake River Plain aquifer that occurs beneath 60 to 275 m of unsaturated zone at the Idaho National Engineering Laboratory (INEL), Idaho (Busenberg and others, 1993).

CFC-Dating Method

Chlorofluorocarbons are stable synthetic organic compounds that are detectable to about one part in 10^{15} (weight) in water and one part in 10^{12} (volume) in air. CFC's were first manufactured in the 1930's, and they are entirely of anthropogenic origin (Lovelock, 1971). The concentrations of CFC's in water vary as a function of the atmospheric partial pressures of CFC's, the water temperature, and the CFC solubility.

CFC-modeled recharge ages refer to the time since the recharge water was isolated from the atmosphere. The CFC-modeled recharge year is determined by comparing the CFC concentration calculated for the soil atmosphere (assuming equilibrium between the soil air and ground water at the recharge temperature) with the atmospheric growth curve (fig. 14).

Detectable concentrations of CFC's are present in post-1940 ground water. The presence of CFC's in ground water indicates recharge after 1940 or mixing of older waters with post-1940 water. The use of CFC concentrations in natural waters as a potential dating tool was recognized in the 1970's (Thompson and Hayes, 1979). CFC's have been used to date ground waters in central Oklahoma (Busenberg and Plummer, 1992).

Busenberg and Plummer (1992) describe special procedures that are required for collection and analysis of water samples containing chlorofluorocarbons. Laboratory analysis uses a purge-and-trap gas chromatography procedure with electron capture detector. The uncertainty in the CFC-modeled age due to analytical uncertainty is less than 1 yr for waters with more than 50 pg/kg (post 1965), but may be several years in waters older than 35 yr.

The recharge temperature is required in CFC dating to calculate the Henry's Law solubility constants that relate ground-water CFC concentrations to air concentrations. Heaton (1981) and Heaton and Vogel (1981) discuss the reconstruction of recharge temperatures from dissolved nitrogen and argon. Small errors in CFC dating are introduced by uncertainties in recharge temperature. (Warmer recharge temperatures lead to younger CFC--modeled ages.) An age error of 2 to 3 yr results from uncertainties of ~2 °C for waters recharged after 1980. CFC-modeled age uncertainties due to uncertainties in recharge temperature are usually less than 1 yr for waters recharged prior to approximately 1975 (Busenberg and others, 1993).

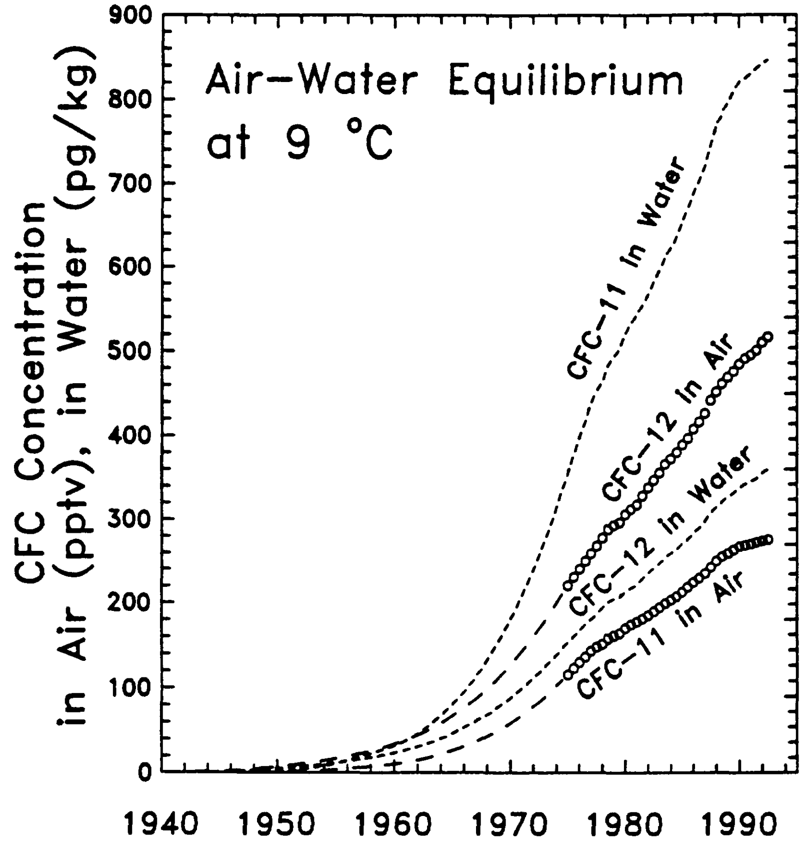


Figure 14. Concentrations of chlorofluorocarbon-11 and chlorofluorocarbon-12 in the atmosphere (Busenberg and others, 1993) and in water in equilibrium with air at 9 Celsius.

Uncertainties result in CFC-modeled ages if (1) the soil air does not annually track the northern-hemisphere continental tropospheric CFC concentrations, such as might occur in deep unsaturated zones (Weeks and others, 1982); (2) there are other sources of CFCs such as from urban air, contamination from sampling equipment, contaminant sources of CFCs in the ground water (Busenberg and Plummer, 1992); or (3) sorption (Ciccioli and others, 1980; Russell and Thompson, 1983) or degradation processes (Lovley and Woodward, 1992) actively remove CFCs from the water.

The CFC-modeled water-recharge age in aerobic environments is regarded as a minimum estimate of time since recharge because of the possibility of contamination of ground water with CFCs, or the possibility of trace introduction of CFCs during sampling. Water-recharge ages can be more uncertain for old waters than for young waters because the CFC concentrations are lower in old waters and more sensitive to contamination.

Ground-Water Ages in the Delmarva Peninsula

Ground water from shallow piezometers and wells in largely unconfined and highly permeable sand and gravel sediments of the Delmarva Peninsula, Atlantic Coastal Plain have been sampled and analyzed for CFC-11, CFC-12, and tritium content. Most of the piezometers were installed to depths of less than 30 m and water samples were obtained through 1 m screened intervals at the bottom of the well. Depths to the water table are generally less than 5 m. Flow paths in this surficial aquifer vary in length from 30 m to several kilometers. The ground water discharges to local streams, wetlands, tidal rivers, and bays.

Ground-water ages derived from CFC-11 and CFC-12 range from pre-1940 to modern. Most of the CFC-modeled ages based on CFC-11 and CFC-12 agree within 3 yr. Differences in CFC-11 and CFC-12 ages larger than 3 yr were attributed to contamination with CFC-11.

Tritium concentrations vary from 0-50 TU and show a strong correlation with CFC-modeled recharge years. Figure 14 shows the measured ^{3}H concentrations after adjustment for radioactive decay (^{3}H half-life = 12.43 yr), plotted versus CFC-modeled recharge year. The expected pattern of the ^{3}H input over Delmarva (solid line, fig. 15) appears to be retained in the adjusted ^{3}H data. Waters older than 40 yr are CFC-free and contain less than one ^{3}H unit, indicating that these waters were recharged prior to nuclear-weapons testing. The period from 1970 to 1990 shows a consistent decrease with adjusted ^{3}H concentrations similar to those expected when the ^{3}H input is unaffected by hydrodynamic dispersion. The dashed lines on figure 15 show the simulated shape and distribution of ^{3}H in Delmarva ground water, if affected by hydrodynamic dispersion (dispersivities of 0.1 and 2 m and an average flow velocity of 1 m/yr).

The mid-1960's adjusted ^{3}H concentrations fall well below the concentrations expected for ^{3}H in 1963-64 precipitation, which exceeded 1,000 TU. Mixing of waters in well screens that intersect portions of the mid-1960's bomb pulse with waters of lower tritium content adjacent to the bomb-pulse waters probably accounts for the observed tritium distribution in mid-1960's waters.

The results from Delmarva indicate that ground-water ages determined from measurements of dissolved concentrations of CFC-11 and CFC-12 can, under optimum conditions, be reliable within several years. Shallow, aerobic ground-water environments in aqui-

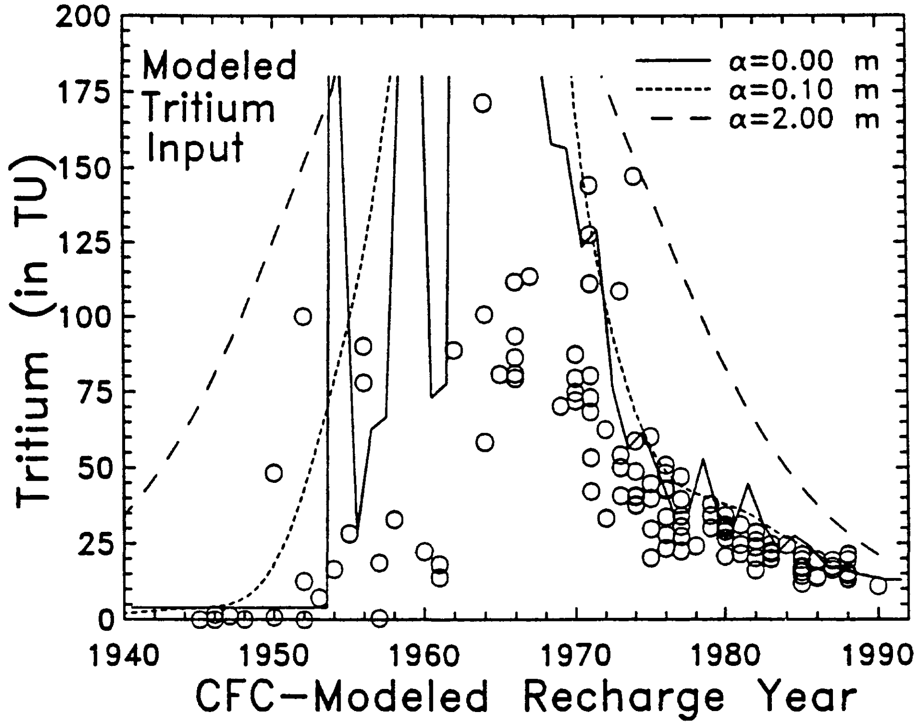


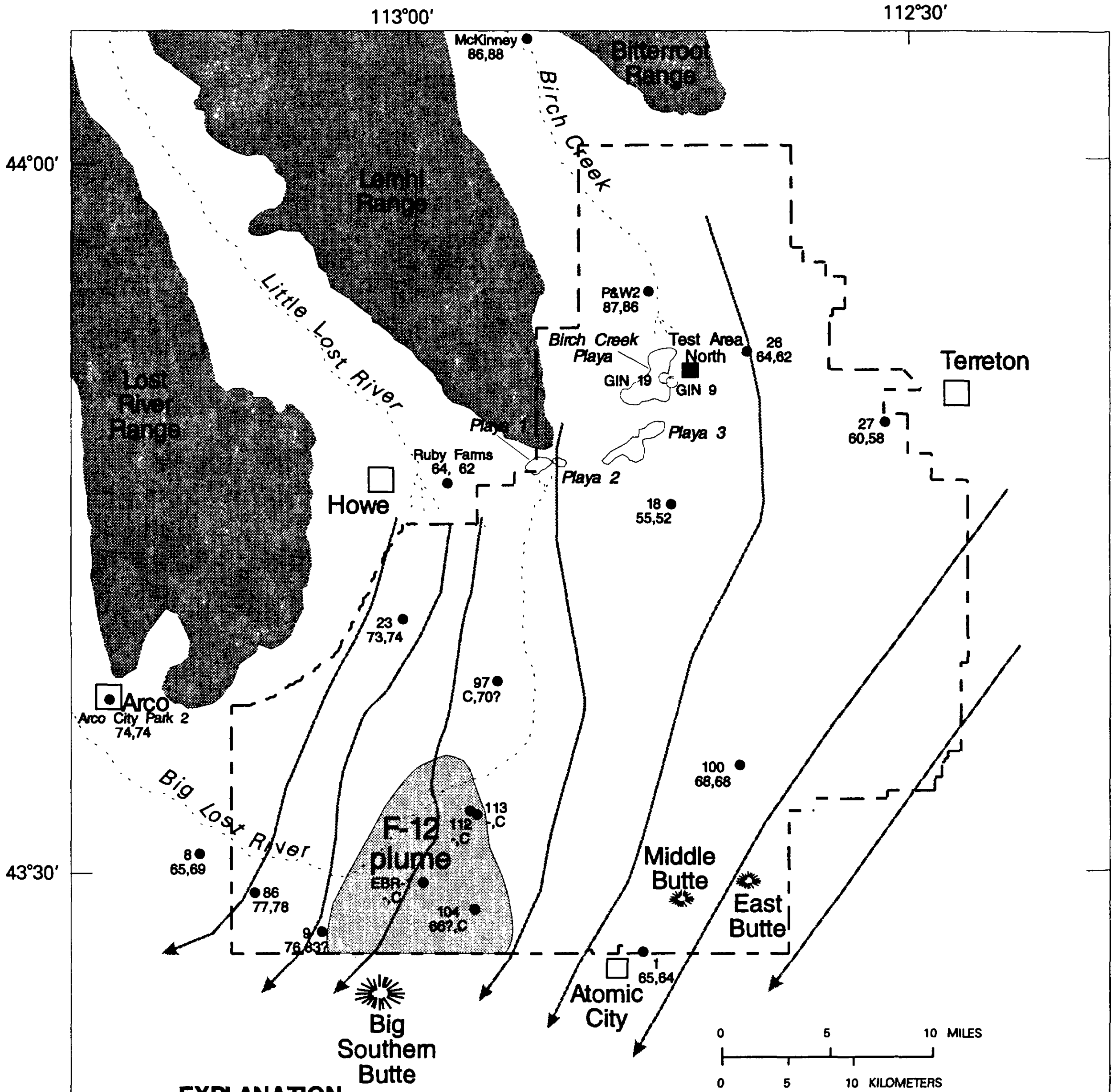
Figure 15. Comparison of reconstructed tritium input in Delmarva ground water as a function of chlorofluorocarbon-modeled age.

fers with low organic matter content, located in rural areas are well suited for CFC-dating applications.

Ground-Water Ages at the Idaho National Engineering Laboratory

The water table of the Snake River Plain aquifer beneath the Idaho National Engineering Laboratory (INEL), Idaho occurs at depths of 60 m (in the northern part) to more than 275 m (in the southeastern part of the site; fig. 16). The CFC concentrations in the unsaturated zone air are significantly different from the northern-hemisphere continental air curve (fig. 14), because of the great thickness of the unsaturated zone (Weeks and others, 1982). Water slowly infiltrating through the deep unsaturated zone no longer maintains equilibrium with the atmospheric concentrations of CFCs.

Water movement in the Snake River Plain aquifer is through fractures in basaltic lava flows and interbedded sedimentary deposits. A significant portion of ground water moves through the upper 240 m of saturated rock (Mann, 1986) where hydraulic conductivities are generally 0.3 to 30 m/dy. The direction of ground-water flow is primarily to the south and southwest with an average hydraulic gradient of 0.7 m/km. Recharge to the Snake River Plain aquifer is principally from rapid infiltration of applied irrigation water, infiltration of streamflow in spreading areas at INEL during flood events, and ground-water inflow through the alluvium in adjoining mountain drainage basins. Direct infiltration of precipitation is believed to be



EXPLANATION

- – – BOUNDARY OF IDAHO NATIONAL ENGINEERING LABORATORY

← GENERALIZED DIRECTION OF GROUND-WATER FLOW--Based on water-level contours constructed from July 1988 water levels

●1 65,64 WELL COMPLETED IN THE SNAKE RIVER PLAIN AQUIFER--Upper entry is the local well identifier; lower entries are the CFC-model recharge dates of CFC-11 and CFC-12, respectively, corresponding in this example to 1955 and 1952. Recharge dates were calculated from the elevation of the well above sea level and a recharge temperature of 10 degrees Celsius. "C" indicates the sample was contaminated with CFC's. "?" indicates questionable dates. "-" indicates date not determined

○ GIN 9 WELL FROM WHICH UNSATURATED-ZONE GASES WERE SAMPLED FOR CFC DETERMINATION--Entry is local well identifier

Figure 16. Location of Idaho National Engineering Laboratory, selected wells, and model chlorofluorocarbon-11 and chlorofluorocarbon-12 recharge dates.

insignificant because of the small annual precipitation on the plain (20 cm at INEL), evapotranspiration, and the great depth to the water table (Orr and Cecil, 1991). The Snake River Plain aquifer eventually discharges to springs along the Snake River downstream from Twin Falls, Idaho, approximately 170 km southwest of INEL.

Busenberg and others (1993) used measurements of CFC-11 and CFC-12 concentrations in ground water and unsaturated zone air at INEL to interpret the recharge mechanism. They show that concentration profiles of CFC-11 and CFC-12 in the unsaturated zone can be explained by gas diffusion processes that alter both the CFC concentrations and ratio of CFC-11 to CFC-12 in the unsaturated zone air. If ground-water recharge occurred by slow percolation through the 60 m thick unsaturated zone at Test Area North (TAN) (fig. 16), water reaching the water table would appear old, with ages based on CFC-11 appearing older than those based on CFC-12 by approximately 7.5 yr. Air at the base of the unsaturated zone contains only 19 parts per trillion by volume of CFC-11 and 137 parts per trillion by volume of CFC-12 (Busenberg and others, 1993). Modern infiltration water in equilibrium with this air would appear to have been recharged in 1963 (based on CFC-11) and in 1970.5 (based on CFC-12) (fig. 14). If significant proportions of waters recharged by slow infiltration in the southern part of the Snake River Plain aquifer at INEL, where unsaturated zones are greater than 60 m thick, the apparent CFC-modeled recharge ages would be older than those estimated at TAN, with differences between ages based on CFC-11 and CFC-12 greater than 7.5 yr.

Figure 16 shows the recharge dates of ground water determined from measurements of CFC-11 and CFC-12. The dates are nearly identical, and inconsistent with ages expected if infiltration waters maintained equilibrium with the unsaturated zone air at the water table. The calculated ages from CFC concentrations range from 4 to greater than 50 yr, with most of the waters having CFC-model ages of between 14 and 30 yr.

The CFC results show that young ground water was added at various locations to the older regional ground water (more than 50 yr) within and outside the INEL boundaries (fig. 16). The Big Lost River, Birch Creek, the Little Lost River, and the Mud Lake area are major sources of recharge to the Snake River Plain aquifer. Apparently, surface waters equilibrate with the atmosphere or within the thin soil zone during recharge events and then move rapidly through the fractured basalts to the water table without further gas-water reequilibration.

Robertson (1974) modeled flow velocities in the Snake River Plain aquifer at INEL in the range of 1.5 to 8 m/d. Busenberg and others (1993) determined a similar range of flow velocities from CFC ages along selected flow paths. Further studies are needed to determine spatial variations in ground-water age as a function of depth, because, unlike the narrow-screened (1 m) wells sampled on Delmarva, the INEL wells draw ground water from the upper 3 to 9 m of the Snake River Plain aquifer, and in one case from the top 60 m of the saturated zone. Additional age-dating studies could improve the definition of the regional flow system in the Snake River Plain aquifer at INEL.

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USE OF LIGHT ENVIRONMENTAL ISOTOPES TO DELINEATE HYDROLOGIC PROCESSES

By Tyler B. Coplen

This topic is addressed in a recent book and interested individuals should refer to:

Coplen, T.B., 1993, Uses of environmental isotopes, *in* Alley, W.M., ed., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 227-254.

URANIUM AND THORIUM SERIES RADIONUCLIDE DISTRIBUTION IN SEDIMENT-WATER ASSOCIATIONS—SURFACE AND GROUND WATER

By Thomas F. Kraemer

Introduction

The naturally occurring radioactive decay chains comprise many elements of vastly diverse chemical and physical properties. These differences cause separation and fractionation of the daughters during weathering, resulting in radionuclide distributions in the aqueous phase that can be used as chemical and isotopic tracers useful in the hydrological sciences. They can also be illustrative of how technologically enhanced quantities of these nuclides may behave in similar environments.

In hot, high-salinity aquifers of the U.S. Gulf Coast, fractionation of decay chain nuclides takes place in response to the extreme conditions found there. The general observation is that the water in the aquifer contains much less uranium than is necessary to support the activity of radium found in the water (Kraemer and Reid, 1984), whereas the radium in the water supports the activity of radon (Kraemer, 1985). This leads to the conclusion that a chemical process is taking place within the aquifer that selectively leaches radium, but not uranium, from solid matrix to solution. This is supported by a number of observations, including: (1) A salinity-radium relationship that indicates that as salinity increases, the reaction rate or efficiency of leaching of radium increases, resulting in higher radium content in the water and (2) bulk sand recovered from these aquifers exhales radon to solution at a much lower rate than sand from a normal surface environment, even though the composition, grain size and uranium content of both are similar. This indicates radium has been leached out of the outer rind of the sand-size grains.

The nature of the reaction selectively leaching radium into formation water is not well known. It has been hypothesized by Kraemer and Reid (1984) that the high formation water salinity causes a more rapid exchange of silica between solution and silicate grain. This exchange "uncovers" radium, which can then escape into solution, where it accumulates due to the high ionic strength of the water. Alternatively, the higher the salinity of the formation water, the deeper into a matrix grain the solution may penetrate to remove radium, resulting in a greater "standing crop" of radium in solution. Whatever the origins, this observation indicates significant water-rock interaction that may be of interest to those seeking to model or understand radionuclide partitioning behavior in high temperature, saline environments.

In the surface water environment, the flux of dissolved uranium and radium isotopes to the ocean from the Mississippi River has been calculated. Long term (~ 4 yr) monitoring of the river has been carried out to examine the seasonal variation of uranium dissolved in the water, and to gain an idea of the present day flux of uranium from the river. An estimated 640 tons of dissolved uranium flows from the Mississippi each year. There is little adsorbed uranium present on suspended-sediment particle surfaces. As a point of comparison, we have calculated that 970 tons of uranium are added to the Mississippi drainage basin each year as a result of phosphate fertilizer application and maximum of 270 tons/yr as a result of application of irrigation water. Uranium is therefore probably accumulating in the soil zone.

Seasonal variation in uranium concentration and flux at the mouth of the river are significant. These values are highest in the summer and lowest in the winter and early spring. There is a correlation between these parameters and the relative proportions of Missouri River and Ohio River water in the Mississippi. During the summer, the uranium-rich Missouri River water makes up a greater proportion of the lower Mississippi water, while early spring water is dominated by low-uranium Ohio River water. Variation of a factor of four are common at the mouth of the Mississippi River during the year.

Radium flux and chemistry has also been examined in the Mississippi River (Kraemer and Curwick, 1991). An estimated 7.7 x 10^{15} Becquerels (1.29 x 10^{14} disintegrations per minute per year (dpm/yr)) of ^{226}Ra and 8.1 x 10^{15} Becquerels (1.35 x 10^{14} dpm/yr) of ^{228}Ra flows from the river in dissolved and adsorbed form. The flux of ^{226}Ra was considerably higher (1.66 x 10^{16} Becquerels (2.76 x 10^{14} dpm/yr)) in the recent past because of a phosphogypsum waste disposal site on the lower Mississippi River whose operation has recently been curtailed. The radium was found to be about equally partitioned between the dissolved and adsorbed phase, both above and below the point of the phosphogypsum waste disposal. Re-equilibration between radium introduced at the disposal site and the suspended sediment and water in the river was found to be rapid, with the distribution coefficients (K_D) returning to upstream values (~4,700) only a few kilometers downstream from the waste site. A rapid radium isotopic as well as chemical re-equilibration is achieved.

Radium isotopes in lakes have been examined and found to be useful tracers of normal limnological processes. After fall overturn, lake water mixes and homogenizes, with the result that the Ra^{228}/Ra^{226} isotopic ratio is uniform throughout the water body. Because of the "aging" of the lake water, the radium isotopic ratio is usually lower than the ratio of water coming into it by way of streams. The half-life of ^{228}Ra is 5.7 yr, and so it decays on a timescale comparable to water residence time in many lakes. During the spring runoff period, water of a higher isotopic ratio flows into the lake where, in some cases such as the Finger Lakes in central New York State, it sinks to a level of equal density in the lake and spreads out laterally as a layer. In most cases this layer would be detectable only with great difficulty, if at all, by conventional techniques because of the similarity of this water to the lake water. However, because of the difference in radium isotopic ratio, the layer is easily detected. It may even be possible to monitor its movement and growth during development.

During the summer, a second feature develops in lakes—the formation of the thermocline. Water above the thermocline, warmed by the sun and less dense than the water below, becomes isolated from the deeper water, with mixing between the two layers largely prevented. Therefore, as surface water flows into the lake during the summer the radium isotopic ratio of the water above the thermocline will change (usually increase) in proportion to the amount of "new" surface water added. The result is a layer of higher radium ratio water above, with lower ratio water below. During fall mixing, it may be possible to observe the mixing dynamics by use of the radium isotopic ratio distribution in the lake.

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GEOCHEMICAL MODELING OF NATURAL AQUATIC SYSTEMS—APPLICATIONS AND LIMITATIONS

By D. Kirk Nordstrom

Introduction

Aqueous geochemical modeling began more than thirty years ago as an attempt to apply more quantitative techniques of chemistry to the interpretation of natural water-rock interactions. Approximately twenty years ago, geochemical modeling was beginning to be applied to hazardous waste investigations. Today, numerous examples of the application of geochemical modeling to hazardous waste studies have been completed. Indeed, much of the support for model and code development is funded and motivated by hazardous waste investigations. This extended abstract briefly summarizes the methods of aqueous geochemical modeling with an emphasis on developments and contributions from the U.S. Geological Survey. Two study sites, one at Stripa, Sweden, and the other near Poços de Caldas, Brazil, are described. This paper also attempts to summarize limitations of aqueous geochemical models. Differences of opinion concerning model usage and model "validation" have arisen between scientists who develop and apply models and regulators who must make decisions based on "expert opinion" and "model results." This problem seems to have arisen from an overemphasis on model development and model validation, rather than an emphasis on understanding natural processes that affect contaminant mobility. These issues are also discussed.

Methods of Aqueous Geochemical Modeling

The word "model" is used so much in so many different contexts that we sometimes forget it refers to a "well-constrained logical proposition, not necessarily mathematical, that has necessary and testable consequences, and [we should] avoid the use of the word if we are merely constructing a scenario of possibilities (Greenwood, 1989)." Consequently, I have defined it as "as a testable idea, hypothesis, theory, or combination of theories that provides new insight or a new interpretation of an old problem" (Nordstrom, 1993). A geochemical model is a theoretical construct that permits the calculation of physicochemical properties of substances and their associated processes in geological systems. Aqueous geochemical models are those used in the interpretation of water-rock interactions.

Several papers have reviewed geochemical models and the interested reader is referred to these for further information (Nordstrom, and others, 1979; Wolery, 1979; Potter, 1979; Jenne, 1981; Nordstrom and Ball, 1984; Nordstrom and Munoz, 1986; Mangold and Tsang, 1991; Plummer, 1992; Wolery, 1992). The present discussion will be limited to a broader overview of the subject emphasizing the major advantages and disadvantages and the inherent assumptions and limitations of geochemical models.

The application of models to water-rock interactions falls into one of three general approaches: forward modeling (or simulation), inverse modeling (or the field mass balance approach), and statistical. Forward and inverse modeling have been described by Plummer (1985, 1992). Forward modeling predicts water compositions and mass transfer that can result from hypothesized reactions and inverse modeling defines mass transfer from observed chemical, mineralogical, and isotopic data (Plummer, 1992). Forward modeling tends to be generic in nature and was developed to answer hypothetical questions such as: what are the thermodynamical and/or kinetic consequences if rock A reacts with fluid B under pressure and temperature conditions C? This approach was pioneered by Helgeson and others (1968, 1969, 1970) for multicomponent, multiphase systems over a wide range of temperature and pressure. Inverse modeling was developed as a deterministic strategy for interpreting groundwater compositions. It attempts to answer the question: what does this set of data mean? Forward modeling is constrained by the assumptions of the modeler whereas inverse modeling is also constrained by the available water chemistry, mineralogy, and isotopic data. Both methods use a chemical model (speciation and mass transfer) and both can utilize thermodynamic or kinetic techniques. The third approach uses statistics, especially factor analysis, to group water chemistry data into statistically significant sets that might be related to hydrogeochemical processes, without employing thermodynamic or kinetic information (Drever, 1988; Puckett and Bricker, 1992). This approach is less constrained than either of the two other approaches and puts even more responsibility on the user to interpret the results. It is not called modeling per se because no laws, theories, or models of physics and chemistry are being used.

Examples of Geochemical Modeling in Nuclear Waste Research

Although there are many examples of geochemical modeling related to nuclear waste research (for example. Jackson and Bourcier, 1986; Trask and Stevens, 1991), only two examples in which the author participated are described below: the Stripa Project in Sweden and the Poços de Caldas Natural Analogue Project in Brazil. The codes used for the geochemical modeling were WATEQ2 and WATEQ4F for speciation calculations (Ball and Nordstrom, 1991), BALANCE and NETPATH for the mass balance calculations (Parkhurst, and others, 1982; Plummer, and others, 1991), and PHREEQE for the thermodynamic mass transfer calculations (Parkhurst, and others, 1980).

The International Stripa Project

The International Stripa Project began as a Swedish-American Cooperative (SAC) Program in 1977 carried out jointly by the USDOE at the Lawrence Berkeley Laboratories and Division KBS of the Swedish Nuclear Fuel Supply Company (now the Swedish Nuclear Fuel and Waste Management Company, SKB or Svensk Kärnbränslehantering AB). The program was designed to develop and evaluate techniques for assessing the thermomechanical, hydrogeological, geophysical, and geochemical properties of granitic bedrock for the safe disposal of high-level radioactive waste. The abandonment of the Stripa iron ore mine in central Sweden provided the opportunity to establish a research site for these purposes. Several additional countries joined the project in 1980 and continued to expand the investigations until its termination at the end of 1991. The main emphasis in the Stripa investigations were the in situ measurements of granitic bedrock properties, ground water properties, heater experiments, tracer experiments, and detection and mapping of fractures.

Hydrogeochemical investigations indicated the presence of slightly brackish water whose origin was unknown. The investigations expanded during the international phase to allow greater expertise and to use more sophisticated geochemical and isotopic techniques to interpret the origin and evolution of the Stripa ground waters. Nearly one thousand samples of water and gases were collected for chemical and isotopic analyses between 1977 and 1987 to a depth of 1,200 m in the pre-Cambrian Stripa granite intrusion.

The ground water composition consists of two general types: a typical recharge water of Ca-HCO_3 type occurring at depths down to about 200-300 m and a deeper Na-Ca-Cl type water of high pH (8-10) reaching a maximum of 1,250 mg/L in total dissolved solids (TDS). Mixtures of the two compositional types appeared that were highly fracture-dependent rather than depth-dependent. Any borehole can vary significantly and erratically in TDS in either a horizontal or vertical direction. The transition from the dilute Ca-HCO_3 water type to the Na-Ca-Cl water type generally corresponds to the change in the average hydraulic conductivity from 10^{-8} m/s to 10^{-11} m/s and lower.

Results of investigations by Nordstrom and others (1989 a, b) demonstrated that leakage of fluid inclusions from the crystalline rock could be a possible source of salt to the Stripa ground waters. The main evidence for this hypothesis is the nearly identical Br/Cl ratio found for both fluid inclusion leachates and ground waters. Mass balance calculations indicate that only a small fraction of the inclusion fluid needs to leak out to obtain the observed ground water compositions. Solubility controls by calcite and fluorite along with feldspar hydrolysis seem to account for the major geochemical processes occurring at the site. With these hypotheses, a geochemical model was constructed that accounts for the ground water chemistry at the Stripa site by selected mineral solubility controls, feldspar hydrolysis, and inclusion fluid mixing with ground waters (Waber and Nordstrom, 1992). The results from these calculations indicate that the ground waters with the highest salt content can be interpreted as a mixture of 4.1 percent inclusion fluid with 95.9 percent dilute ground water along with large amounts of calcite precipitation and plagioclase dissolution to give the low partial pressures of CO_2 and the high pH values. Preliminary results demonstrate that the model is thermodynamically feasible but when isotopic results are included in the mass balance, a model solution is not uniquely defined. One important modeling result was the elimination of Holocene-entrapped seawater as a possible source of the salinity. On the basis of mass balance modeling for both major ions and stable isotopes in water and sulfate it has been shown that mixing of present-day or Holocene seawater cannot account for the composition of the Stripa ground waters (Fontes, and others, 1989; Waber and Nordstrom, 1992).

Additional results from the Stripa studies include the first detailed investigation of radioisotopes and gases at depth in a granite (Andrews, and others, 1989 a, b; Loosli, and others, 1989). Calculations of subsurface production of tritium based on both theory and in situ measurements of neutron flux were considered as possible explanations for the clearly detectable tritium at several hundred meters depth (Andrews, and others, 1989c). Several methods of calculating ground water ages from radioisotopes were attempted with the conclusion that the in situ radionuclide production rates, the mechanisms of rock to water transfer, and the flow paths of the ground water can seriously interfere with any quantitative dating technique. Different radioisotopes will give different dates, none of which may relate to the groundwater residence time. Such conclusions can confound attempts at using radioisotope dating as an integral part of geochemical modeling. This study was the first comprehensive study of isotopes and gases in a crystalline rock and did much to extend our understanding of water-rock interaction in granitic ground waters.

The useful aspects of geochemical modeling for the Stripa hydrogeochemical investigations were (1) it integrated conceptual models, experimental data, and field data, (2) it allowed the explicit testing of the thermodynamic consequences of possible conceptual models of water-rock interactions, and (3) it provided a means of testing and eliminating possible hypotheses for the origin and evolution of the ground waters. It is also important to note that the geochemical modeling could not have been as useful without the collection of a considerable amount of field data and thought and discussion about the data. Sources for the salinity of the water had to be considered and debated before quantitative models could be employed successfully. Fluid inclusion leaching experiments and isotopic data such as ^{36}Cl shed new light on the investigations, independent of any modeling results.

The International Poços de Caldas Project

The Poços de Caldas Natural Analogue Project was initiated to study and assess the hydrobiogeochemical processes in a naturally-radioactive environment that may have relevance to the safety assessment of radioactive waste disposal. Testing and evaluation of hydrogeochemical models and investigations of a redox boundary and its effect on radionuclide transport were major goals of the program. The two study sites, Morro do Ferro and Osamu Utsumi mine, are located in the state of Minas Gerais, Brazil, a region of high natural radioactivity. The Osamu Utsumi open-pit uranium mine contains a prominent redox front and Morro do Ferro contains an unmined high-grade thorium deposit. The rocks at the Osamu Utsumi mine are primarily phonolite volcanics that have undergone hydrothermal alteration and mineralization followed by about 75 million yr of weathering. The alkalic igneous complex began with a high concentration of alkalis that was further enriched by the hydrothermal alteration and weathering so that in the oxidized portion of the rock only significant amounts of potassium remained in the rock to be weathered. The ground waters are generally of a K-Fe-SO_4-F type derived from the dissolution of potassium feldspar (predominately orthoclase), fluorite dissolution, and pyrite oxidation. Notable aqueous concentrations of barium, zinc, aluminum, manganese, and silica were also obtained.

A conceptual model of mineral reactions was proposed from considerations of ground water compositions, mineralogic data, and ion plots. These ideas were formalized with speciation calculations for saturation indices and with simultaneous-mass-balance calculations. The results gave a reasonable model with the chief uncertainties dealing with the relative importance of illite dissolution relative to orthoclase dissolution as a source of potassium, chlorite dissolution relative to smectite dissolution as a source of magnesium, and kaolinite precipitation relative to gibbsite and chalcedony precipitation as a sink for aluminum and silica. These uncertainties, however, did not change the main features of the model: (1) dissolution of orthoclase, fluorite, calcite, albite, chlorite (or mixed-layer clays), and manganese oxides; (2) oxidation of pyrite and sphalerite; (3) barium solubility control by barite; (4) precipitation of kaolinite, cryptocrystalline silica and/or gibbsite, and ferrihydrite; and (5) high partial pressures of CO_2 derived from the soil zone. These results were tested with forward modeling by using the PHREEQE program and it was found that the pH, pCO_2, and water chemistry could be reproduced using the mass balance model results and the same set of thermodynamic variables as were used in the speciation calculations.

As with the example with Stripa, it was found that geochemical modeling was extremely useful in integrating the data and testing hypotheses but that no unique model solution was possible due to incomplete and inadequate field and isotopic data.

Two other examples of the application of geochemical modeling to the interpretation of ground-water chemistry include the regional aquifer of the Madison Limestone (Plummer, and others, 1990), a classic example of inverse modeling on a large scale, and the mass-balance model of the Rapakivi granite aquifer, Finland, where low-level radioactive waste will be stored (Nordstrom, 1986, 1989).

Modeling Limitations

The limitations and uncertainties of geochemical modeling fall into two main areas, those associated with input data and those associated with conceptual misunderstandings of the modeler. The first area covers uncertainties in the analytical data, the mineralogical data, the thermodynamic data base, and the chemical model for speciation and activity coefficients. These uncertainties can and are being refined by improving the field and analytical techniques, improving the reliability of the thermodynamic data, and improving the chemical models for electrolyte solutions. Furthermore, sensitivity analyses can provide insight into the major sources of error and can determine where improvements are most needed. For example, the effect of analytical and thermodynamic errors on computed saturation indices for calcite, fluorite, barite, gibbsite, and ferrihydrite for a set of acid mine waters from California and the Stripa ground water samples was investigated by Nordstrom and Ball (1989). They concluded that for these mineral saturation indices, the analytical errors in the water analyses were greater than those in the thermodynamic data.

The second area of model uncertainty, that associated with conceptual misunderstandings, has to do with the application of hydrogeochemical knowledge and experience to the problem at hand. This topic includes: what assumptions are made about what minerals reach equilibrium and which ones do not; what the relative reaction rates are for mineral dissolution and precipitation reactions under different sets of conditions; what redox reactions are significant and which ones are not; what role organic reactions play; to what extent do different aquifer waters mix; are there hydrological heterogeneities that affect water chemistry; does hydrodynamic dispersion play a role; and are there geological complexities. Hydrogeochemical processes can be exceedingly complex and their interpretation requires a considerable amount of training and experience. This point has been made rather frankly by Mercer and others (1982): "Inappropriate model use is the major factor that contributes to a lack of credibility in model results. This misuse is usually related to the experience of the user." Of course it is not just user misuse that is the only cause of uncertainties. It is simply uncertain knowledge; much research is currently being conducted on mineral dissolution and precipitation rates, surface chemistry, redox reaction rates, applicability of equilibrium

Furthermore, even if we had most of the answers, there are always limitations with regard to the adequacy and completeness of the field information. The heterogeneities and complexities of the natural environment tend to overwhelm our ability to sufficiently sample and characterize it.

Regulatory agencies have had to rely on models to make predictions of performance assessment for nuclear waste and other hazardous waste repositories for hundreds to thousands to millions of years into the future. Since the actual performance of repositories over these time frames cannot be tested beforehand, a considerable amount of weight is given to the result of model calculations. Consequently it becomes important to know how reliable are the model estimates. There is now a major emphasis on "model validation." At this point, a difference of opinion has arisen between the scientist, the engineer, and the regulator regarding the meaning of validation. Validation tends to imply two things that science cannot guarantee: the concept of an established truth (or falsity,) and the concept of official confirmation. Established truth is implied because we assume as much when we validate a parking ticket or we validate a will. When it is done, if done properly (eye-witness and notary public, if necessary), it is proven correct and should stand up in court. Science, however, goes deeper than common sense or legal sense. It develops fundamental ideas, concepts, theories, models, and laws about the nature of physical reality where the language is different, the skills are complicated, the degree of precision needed is more detailed, and the amount of uncertainty much greater. At best, we can only estimate the probability that a proposition may be judged true or false. When a scientist tests a model and finds that a prediction works, he or she is usually referring to a logical prediction, i.e., the deduced consequence of a model. When a regulator speaks of model prediction, he or she usually refers to the common usage of temporal prediction, that is, predicting the state of a system in some future time. Science does not do temporal prediction per se but only as an outcome of logical prediction (Strahler, 1992). Science can only predict outcomes when the auxiliary assumptions are well-known, the scientific principles well-established, and then only for the specified conditions. "Actual" conditions are unknown. In futuristic scenarios, the most likely specified conditions for the state of the system are not amenable to model estimates (or perhaps even scenario guesses). History would indicate that it is what we don't anticipate that could most likely happen.

Concluding Remarks

Regulatory agencies frequently use geochemical models as an aid in environmental decision-making. The results range from helpful to meaningless, depending on the perspective of the regulatory agency, the strategy and experience of the modeler, the adequacy and reliability of the field data, the recognition of model assumptions and uncertainties, and the amount of critical peer review. Overemphasis on model development and model validation has often detracted from the main goal of understanding the processes controlling the mobility of contaminants in natural aquatic systems. Testing geochemical models with field data to assess their "validity" is an essential part of scientific research, but it really tests their consistency with field data, not necessarily their proximity to truth. A model that is consistent with field data, yet incorrect, is certainly conceivable. Science advances by testing the deduced consequences of theories and models, checking for logical consistency, applying skeptical criticism and peer review, and finally arriving at an informed judgement. Improvements to geochemical models is an iterative process by which we gradually gain better knowledge of water-rock interactions by collecting more field data of a higher quality. Inverse modeling techniques can contribute significantly to building this knowledge, especially when complemented with uncertainty analysis. Geochemical models are a useful guide to our thinking and our understanding of natural processes, but attempts to validate them for regulatory purposes are inappropriate because this leads to public misconceptions about scientific and technical capabilities.

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AN OVERVIEW OF UNSATURATED-FLOW THEORY AS APPLIED TO THE PHENOMENA OF INFILTRATION AND DRAINAGE

By D.A. Stonestrom

Introduction

Low-level radioactive waste (LLRW) is produced by nuclear-based power generation and other industrial, scientific, and medical activities. The measurement and prediction of infiltration and drainage have been relevant to LLRW disposal since such waste was first interred in shallow landfills. The U.S. Nuclear Regulatory Commission recommended that LLRW-disposal sites be located in unsaturated zones (Healy, 1989). Additionally, the Low-Level-Waste-Policy Amendments Act of 1985 directed each State to designate a site for the disposal of LLRW or to form a compact with other States to designate a site. Because of this, few a-priori limitations can be imposed on the climatic and geologic settings in which unsaturated-zone processes must be considered (Ahearne, 1993).

This paper provides a brief summary of technical issues pertinent to the measurement and prediction of infiltration and drainage. Gaps in the understanding of relevant processes and unresolved technical issues facing practitioners are illustrated by questions that reflect the rich diversity of contemporary activity in unsaturated-zone research. Limitations of space preclude comprehensive coverage of the depth and breadth of this activity. Such reviews can be found elsewhere (for example, see Gee and others, 1991). Instead, an attempt is made to set the stage for the presentations to follow by posing questions, exemplified by the papers in this session, that represent the main challenges to the successful treatment of unsaturated flow. These questions fall into three interrelated groups expressed by the following broad queries: (1) How complete is our knowledge of the relevant processes and of their governing equations? (2) How complete is our knowledge of the parametric functions appearing in those equations? and (3) How is the complexity represented by ordinary field settings to be dealt with?

How Complete is Our Knowledge of the Relevant Processes and of Their Governing Equations?

In the simplest case, the unsaturated zone is isothermal and homogeneous, biotic influences are insignificant, the gas phase is of negligible importance, and interactions between solids and liquids do not require explicit consideration (that is, the porous medium can be considered to be nonswelling and nonreactive). How well do we understand flow in this simplest case? The Richards equation, which describes such an idealized system, is the main paradigm on which measurement and prediction of infiltration and drainage is based. Yet few critical tests of the applicability of the Richards equation have been attempted (Nimmo, 1990).

In tests by C. Ripple, K. Akstin, and myself (all of the USGS), solutions containing 0.01 M Ca^{2+}, 0.005 M SO_4^{2-}, and 0.005 M SeO_4^{2-} were applied at constant rates that were less than saturated hydraulic conductivity (Ksat) to the tops of air-dry, 0.05 m-diameter, 0.7 m-tall columns of uniformly packed glass beads and soils. Tensiometers monitored matric-pressure histories at several depths after passage of the wetting fronts. Experiments were terminated before wetting fronts reached the bottoms of columns.

The Richards equation predicts that matric pressures above the wetting fronts will become constant under these conditions. Contrary to these predictions, however, measured values of matric pressure passed through maxima then decreased continuously as wetting fronts moved down the columns. This nonideal response was observed in a silt loam, a sandy loam, two sands, and monodisperse glass beads (fig. 17). At an infiltration rate equal to 70 percent of Ksat, values of matric pressure at 2, 5, and 8 cm depths in the glass-beads column decreased an average of 52 percent from their respective maxima in about 3 hours. The nonmonotonic response was less pronounced in the soil columns but still significant at probability levels exceeding 90 percent for all rates examined (which spanned 3 to 59 percent of Ksat for Oakley sand). Matric-pressure reversals were larger, and corresponding maxima higher, when a given rate was preceded by a series of stepwise-increasing rates than when the same rate was applied as a single step to an initially air-dry column (fig. 18). Tests of possible causes produced no evidence to support hypotheses involving trapped-air dynamics, convective air flow, particle rearrangement, or experimental artifacts. These results raise questions

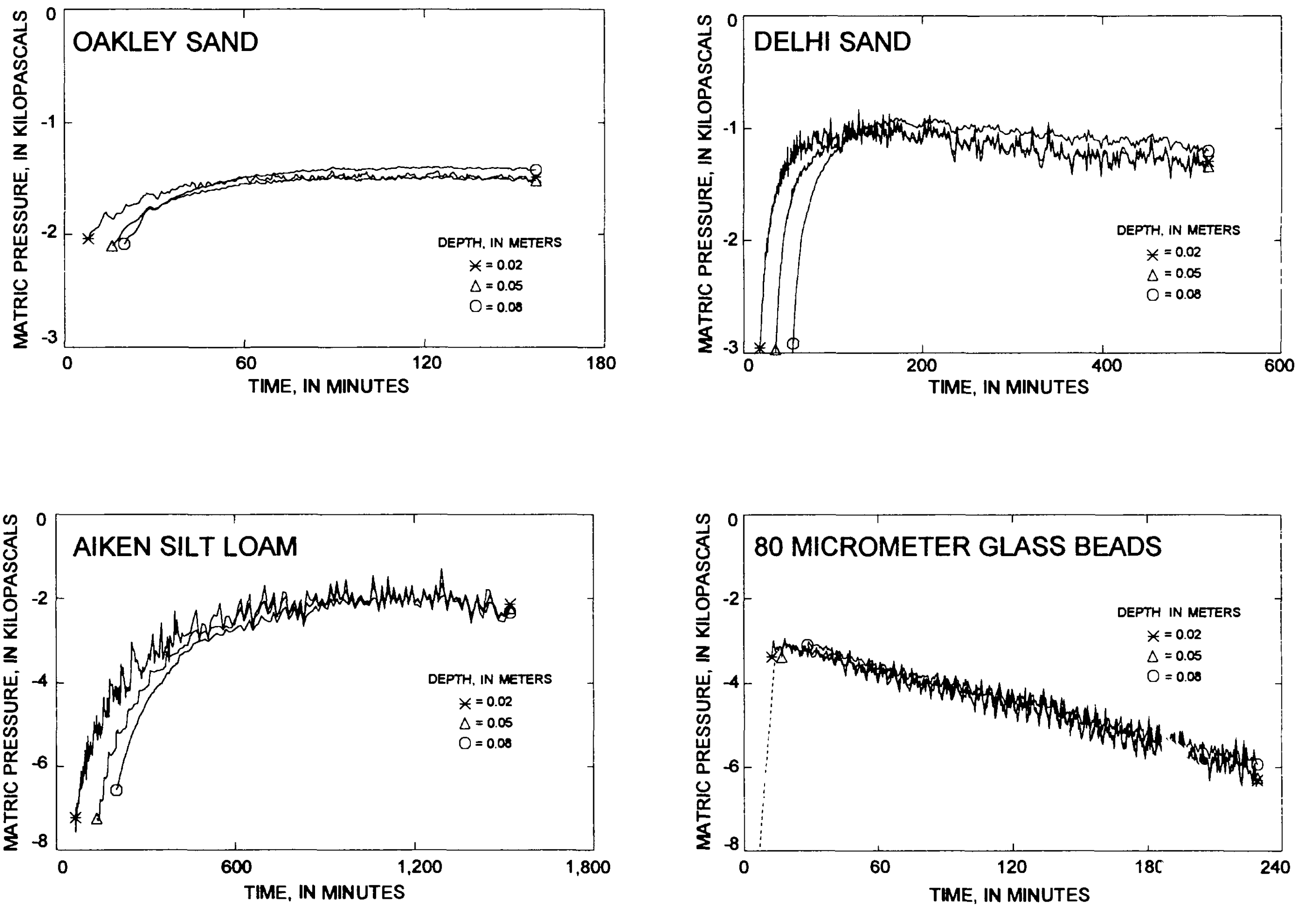

Figure 17. Nonmonotonic matric-pressure histories during constant-flux, isothermal infiltration into soils and glass beads. The constant applied flux, relative to the respective saturated hydraulic conductivity, was 10 percent for Oakley sand, 23 percent for Delhi sand, 47 percent for Aiken silt loam, and 70 percent for glass beads. The dashed line on the glass-beads plot approximates the unmeasured, early history of the run.

about the ability of Richards-based theory to predict the course of infiltration, including the initiation of runoff (Stonestrom and Akstin, 1994).

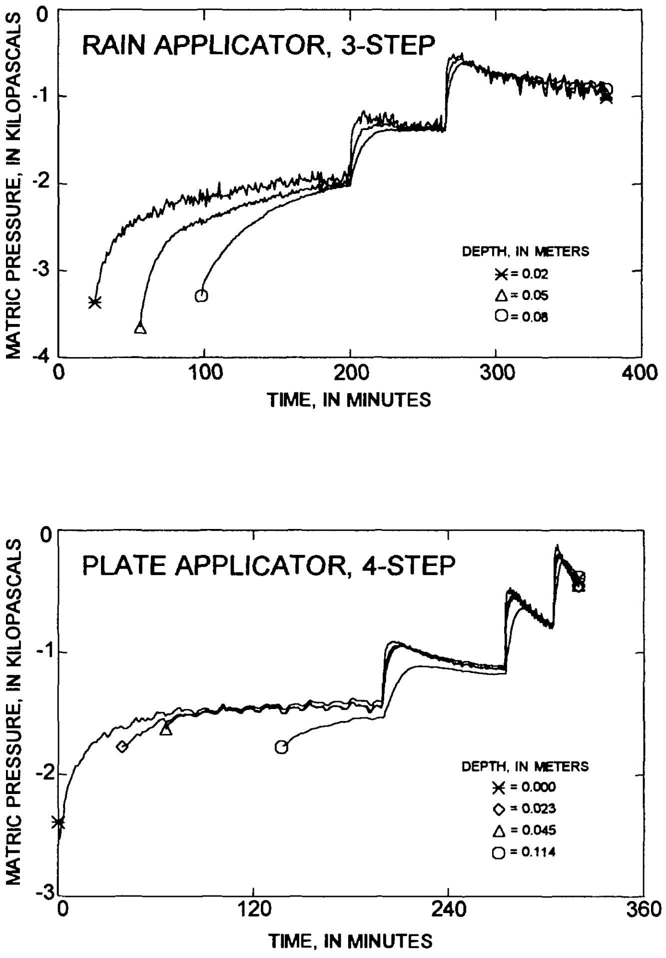

Figure 18. Nonmonotonic matric-pressure histories during stepwise-increasing, constant-flux infiltration into Oakley sand (Stonestrom and Akstin, 1994). *Top.* Fluxes of 3, 8, and 21 percent of saturated hydraulic conductivity were applied to the top of the column through a rain simulator. *Bottom.* Fluxes of 3, 8, 21, and 59 percent of saturated hydraulic conductivity were applied to the top of the column through a porous ceramic plate.

The generalization of unsaturated-flow theory to infiltration and drainage at real-world LLRW sites raises questions about the additional processes operative in nonideal cases. How well are the multiphase flow aspects of infiltration and drainage understood and how are they to be treated? Such aspects include the trapping of nonwetting-phase fluids (Stonestrom and Rubin, 1989) and the convective flow of unsaturated-zone gases (Weeks, these proceedings). The proper treatment of barometrically driven processes is a topic of active debate (Massman and Farrier, 1992). The role these processes play in water movement is poorly understood.

Questions arise because of the presence of yet other processes. Andraski's (these proceedings) treatment of water movement at an arid LLRW disposal site underscores the importance of thermally driven flow. How sound are current theories of nonisothermal flow, and how can such theories be incorporated into predictive models? How well are solute-solid interactions (including shrinking and swelling) understood? Biotic processes strongly influence infiltration and drainage. Lysimeter studies near Richland, Washington, have demonstrated that vegetation can play a dominant role in determining recharge (Gee, these proceedings).

Additional biotic processes may need to be considered. For example, microbial cells and the polysaccharides these cells produce can strongly influence water movement by altering hydraulic conductivity. The development of equations governing such processes is an area of active research (Taylor and others, 1990).

How Complete is Our Knowledge of the Parametric Functions Appearing in Theories of Infiltration and Drainage?

This category of questions is closely related to the previous one because many processes that are not considered explicitly in simplified models appear implicitly through their influence on the parametric functions of the models. That hysteresis occurs in key parametric functions is well established. For example, figure 19 illustrates differences in the water-content dependence of matric pressure during wetting as opposed to drying. Even for flow involving only wetting or only drying, matric pressure may not depend solely on water content, but also on the rate at which the water content is reached (Constantz, 1993). Hysteretic aspects of parametric functions are incompletely understood and characterized, making effective treatment of hysteresis a continuing challenge (Nimmo, 1992).

To what degree are parametric functions dependent on the scale of observation? The scale at which hydraulic properties should be measured in the field is an unresolved issue of central importance (Neuman, these proceedings).

Apart from the fundamental questions raised above, the measurement of parametric functions at any scale presents significant challenges. The strong nonlinearity in the water-content dependence of hydraulic conductivity creates substantial problems for measurement and prediction (fig. 20). Nimmo (these proceedings) addresses the question of how measurement techniques that were developed for root-zone measurements can be adapted to materials and conditions existing in LLRW disposal sites. Gravels and compacted clays, and extremely low water contents have received scant attention by traditional soil-physics and agricultural disciplines.

How can the Complexity Represented by Ordinary Field Settings be Dealt With Effectively?

The third group of questions involves the complexity of the operative processes and parametric functions in actual field settings. A main source of complexity is the typically heterogeneous distribution of hydraulic properties in space. The field and theoretical studies of Wierenga (these proceedings) and Gelhar (these proceedings) raise questions about whether property heterogeneity can be adequately characterized by point measurements. Hills (these proceedings) challenges the conventional wisdom that detailed representation of heterogeneity necessarily leads to improved performance of predictive models.

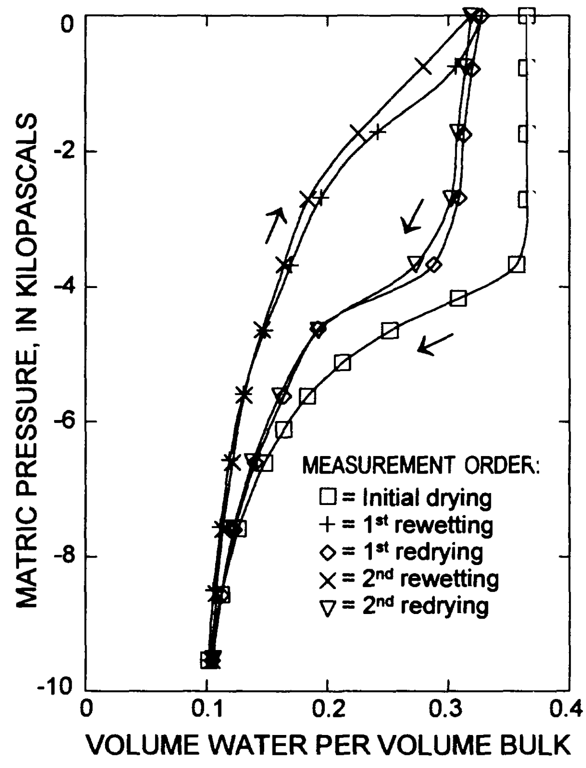

Figure 19. Hysteretic water-content dependence of matric pressure in Oakley sand, a nonswelling soil, under isothermal conditions (Stonestrom, 1987).

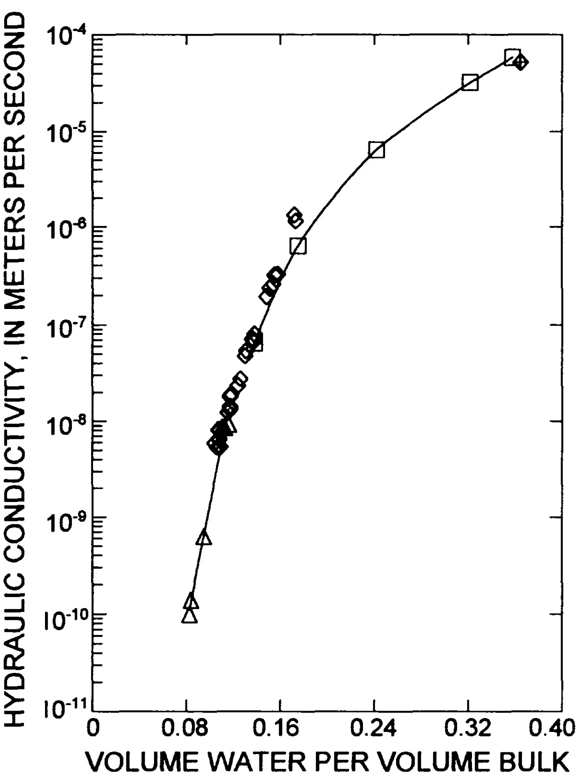

Figure 20. Water-content dependence of hydraulic conductivity in Oakley sand. Squares and triangles, respectively, show data of C. Ripple and J. Nimmo (Nimmo and others, 1987). Diamonds show data obtained by the author (Stonestrom, 1987).

Another type of complexity is introduced by preferential flow. Various conditions produce flows that bypass substantial parts of the unsaturated zone. Fractures, ped boundaries, and similar planar features can cause preferential flow (Weeks, these proceedings). Root channels, burrows, and other biologically produced macropores can also cause preferential flow (Edwards and others, 1988). Topographic and stratigraphic features can produce focused recharge (Winter, 1983) or funnel flow (Kung, 1990). Additionally, some studies indicate that wetting fronts might be inherently unstable, tending spontaneously to break up into fingers (Selker and others, 1992).

Other questions arise from the complex forcing at the land-atmosphere boundary. The near-surface environment responds to infiltration and drainage events on relatively short time scales. Surface-imposed fluctuations become attenuated with depth (fig. 21). How can surface forcing be integrated to produce accurate long-term predictions of system response? In arid regions, net recharge is often the difference between two nearly equal precipitation and evapotranspiration amounts. In such situations, water-balance estimates tend to be dominated by error (Gee and Hillel, 1988). Alternate approaches based on the movement of environmental tracers are being developed (Prych, these proceedings). The generality of tracer-based methods in various settings remains to be seen.

Concluding Remarks

The disposal of low-level radioactive waste in unsaturated zones requires the measurement and prediction of infiltration and drainage. Incompletely resolved technical issues facing practitioners can be grouped into three nonexclusive categories reflecting questions about (1) the completeness of current knowledge about the relevant processes, (2) the ability to measure and model parameters appearing in the equations that describe these processes, and (3) the treatment of the complexity inherent in field settings. A multidisciplinary research approach is clearly required. Better understanding of unsaturated flow will lead to improved placement of future disposal sites and to improved monitoring of existing sites.

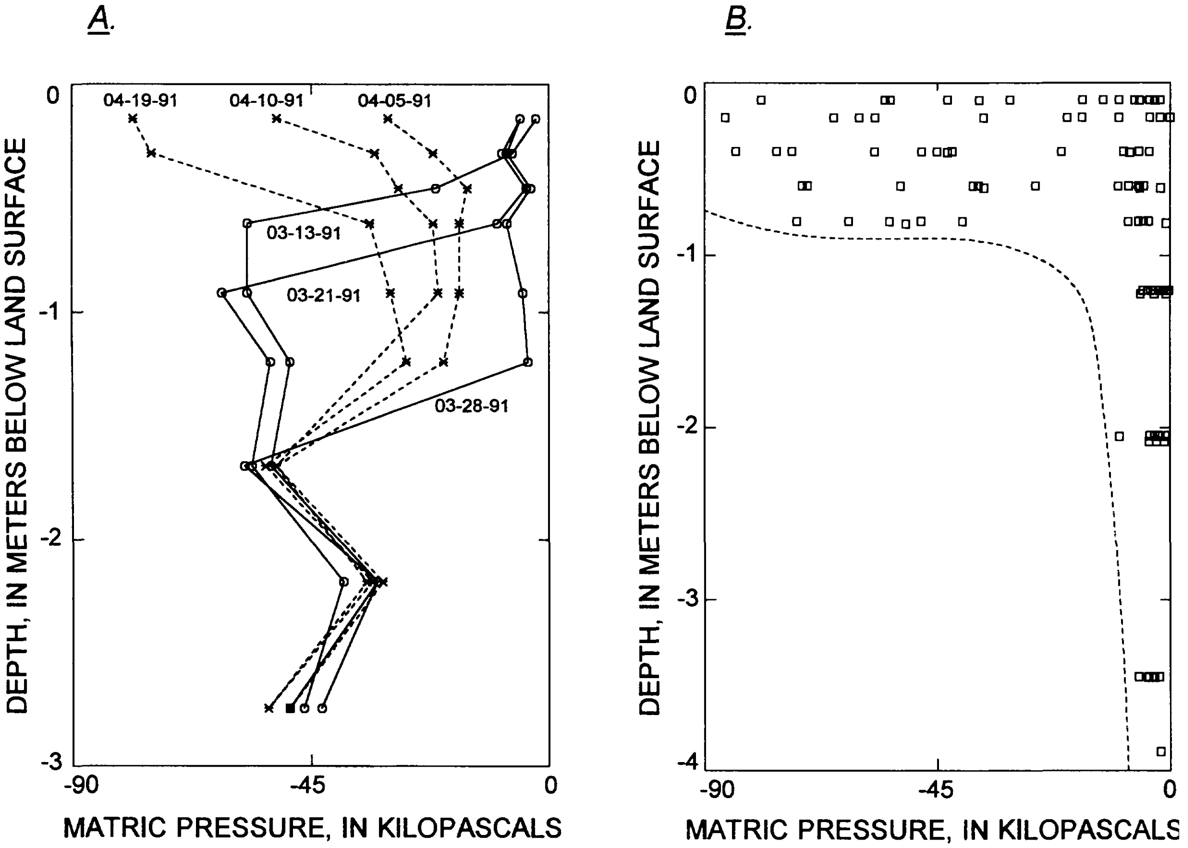

Figure 21. Attenuation with depth of temporal variations in matric pressures beneath uncultivated fields near Merced, California, under natural rainfall conditions (unpublished data of Arthur White, Marjorie Schulz, and Alex Blum, 1992, U.S. Geological Survey, 345 Middlefield Road, Menlo Park, California). Harden (1987) shows locations of these chronosequence sites. *A*. Matric-pressure response of a Modesto chronosequence site to a series of storms that followed a 2-month dry period. About 160 millimeters of rain fell between February 27, 1991, and March 27, 1991, producing a wetting front that advanced to a depth of about 1.3 meters (solid lines). The rains ended on March 27, 1991. Subsequent evapotranspiration produced the drying profiles shown by the dashed lines *B*. One-year record of matric pressures at a Turlock Lake chronosequence site. The dashed line approximates the lower limit of negative matric-pressure values during the period of measurement. The strong attenuation of temporal fluctuations at a depth of about 1 meter corresponds to the presence of an argillic horizon.

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MEASUREMENT OF UNSATURATED ZONE PHYSICAL CHARACTERISTICS AND WATER FLUXES

By John R. Nimmo

Introduction

The most important problems concerning the movement of water and other substances near buried radioactive waste require knowledge of hydraulic conductivity (K) and the relation between water content (θ) and matric potential (Ψ). Examples include the determination of the recharge flux that would carry contaminants to an aquifer, the transient fluxes and moisture contents near buried waste in the shallow unsaturated zone, and the effectiveness of barrier materials used to control or inhibit flow. These problems require accurate and reliable knowledge of extreme dry as well as wet conditions, of deep layers as well as the root zone, of unusual materials such as dense clays and gravels, and of materials modified by construction procedures.

Measurement techniques for these properties developed for agriculture and other purposes are not always adequate, as they frequently emphasize root-zone measurements at high water content. This report describes several methods developed recently for K and θ-Ψ relations, with emphasis on their adequacy for radioactive waste applications.

Unsaturated K measurement

Deep in the unsaturated zone, the fluctuations in moisture that occur near the surface are damped out, possibly creating a zone of uniform c in which the flow is steady and driven by gravity. Gardner (1964) pointed out that K measurement in such a zone at the value of θ that exists in the field can directly indicate the long-term average recharge rate. A major difficulty in doing so is that the K values corresponding to typical recharge rates are so low (for example 3×10^{-8} cm/s, corresponding to recharge of 10 cm/yr, that standard gravity-driven steady-state flow techniques cannot measure them. Alternative methods have inferior accuracy. The widely used technique of computing K(θ) from θ(Ψ) data often is in error by an order of magnitude or more, as can be seen from the tests of Yates and others (1992). The one-step outflow method (Gardner, 1956) can entail nearly order-of-magnitude uncertainty, as the computational-method comparisons of Valiantzas and Kerkides (1990) suggest. To achieve steady-state accuracy (about 10 percent or less) at K values relevant to recharge rate determination, Nimmo and others (1987) developed the steady state centrifuge method (SSCM). Figure 22 shows a recently modified version of the apparatus (Nimmo and others, 1992). Adjustments of centrifuge speed and reservoir configuration can vary the compressive force on the soil to reproduce the overburden pressure of the field position of the sample. Corrections for temperature differences between field and laboratory may sometimes be important.

After steady state fluxes have been measured, K is calculated using Darcy's law with centrifugal replacing gravitational force. The matric potential gradient can be negligible compared to centrifugal force at high speeds, but it can essentially cancel the centrifugal force at low speeds. The minimum speed to assure domination of the centrifugal force depends on the medium, and is generally greater with finer texture (Nimmo and others, 1994). The speed must be chosen carefully to exceed this minimum and to achieve an appropriate degree of compaction.

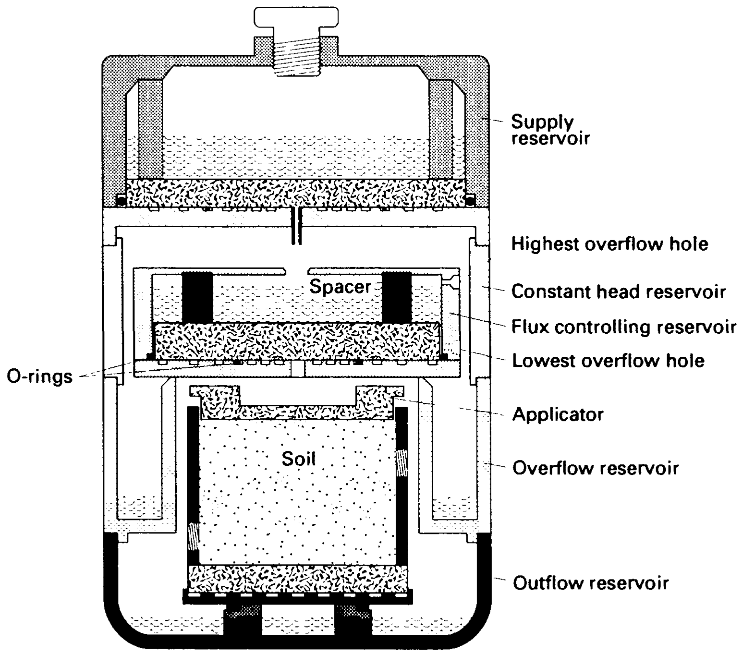

Figure 22. Apparatus that fits in a 1-liter centrifuge bucket for steady-state measurement of low values of unsaturated hydraulic conductivity with forces as great as 2,000 g. Porous ceramic controls flow out of the upper reservoirs. The ceramic applicator receives water at a constant rate and spreads it for even infiltration into the soil. The various reservoirs are separated between centrifuge runs for weighing to determine the flux and water content in the soil.

Saturated K

Centrifugal force can also aid the measurement of small values of K_{sat} (Nimmo and Mello, 1991). The simplest method uses apparatus similar to that in figure 22, but without the supply reservoir and with an extension of the soil retainer holding water ponded above the soil. Repeated measurements of the declining water level made between centrifuge runs provide data that can be reduced to Ksat using a centrifugal analog of the gravitational falling-head formula. The lack of additional reservoirs above the soil frees up space to install a linear displacement transducer that, with a specially modified centrifuge (Nimmo, 1990), can determine the degree to which the soil is centrifugally compacted during the measurement.

Water Content-Pressure Relations

Several available methods can, at least for the drying direction and the wet portion of the range, reasonably produce the $\theta(\Psi)$ data needed for modeling transient flow near shallow buried waste. The submersible pressure outflow cell (SPOC) method originated by Constantz and Herkelrath (1984) is especially versatile and accurate. Figure 23 shows a SPOC assembly designed for highly automated operation. A computer monitors the water content to test against an equilibration criterion at each Ψ value of the measurement sequence. Computer-controlled regulators permit succeeding Ψ values to be set without human intervention. This system is also especially well suited to one-step outflow measurements of unsaturated K and diffusivity.

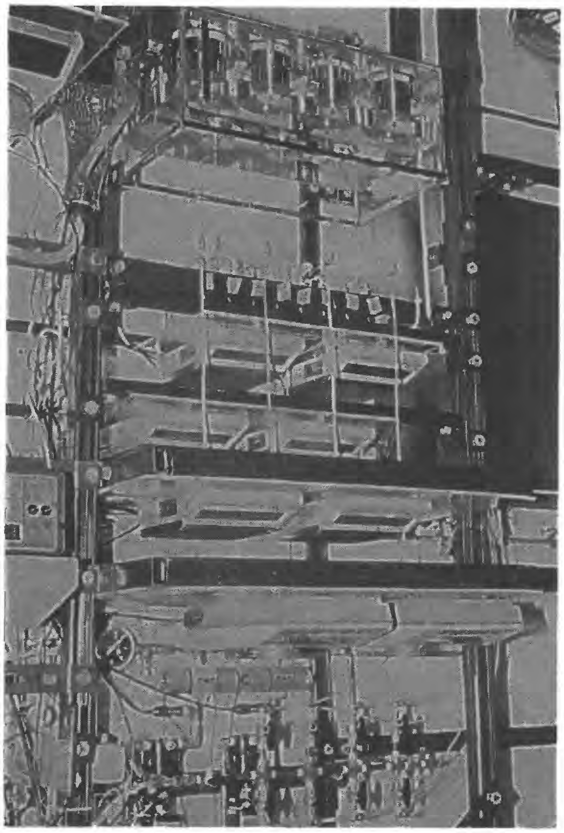

Figure 23. Submersible pressure outflow cells (near bottom), submerged in a water bath during moisture retention measurements. Water in the pores of the sample inside the cell equilibrates with the water pressure in the bath through a porous disk on the underside of the cell. Each cell hangs from a hook connected to an electronic balance that determines the weight used to compute water content. To establish each desired Ψ value, air at a controlled pressure enters the submersible pressure outflow cell through a 1.57-millimeter-diameter coiled polyethylene tube that negligibly influences the measured weight.

Even with efficient measuring techniques, it is often necessary to apply theoretical developments that can extend the data beyond what was measured. For the case where the low-water content range is important but only high-θ data are available, a model of Rossi and Nimmo (1994), designed to realistically represent the entire $\theta(\Psi)$ relation from saturation to oven-dryness, can extrapolate to the range of interest. For the case where hysteretic $\theta(\Psi)$ relations are important but the wetting data are difficult to measure, the semiempirical model of Nimmo (1992) can produce a complete wetting curve based on a drying curve and two measured points on the wetting curve.

Selected Results and Interpretation

In measurements on core samples from a site in the Palouse region of southeastern Washington, the SSCM has produced measurements (fig. 24) that can be interpreted as recharge rate indications (Nimmo and others, 1994). Water contents and textural measure-

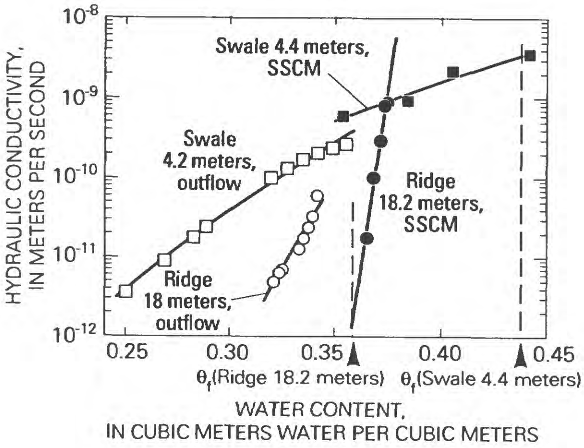

Figure 24. Unsaturated hydraulic conductivity by two different methods versus water content for samples from two locations (ridgetop and nearby swale) at the Palouse site. Reading off the steady state centrifuge method K values corresponding to the field water contents of the samples (ϑ_f) indicates a recharge rate of about 11 centimeters per year in the swale, less than 0.1 centimeter per year on the ridge. The steep slope of the ridge $K(\theta)$ curves highlights the need for accurate measurements; use of the less accurate one-step outflow results would produce a recharge estimate orders of magnitude greater.

ments suggest that the samples were taken from zones of constant downward flow, as required for the interpretation of recharge rates from K(θ) measurements. Although these results come from only two samples and so cannot provide firm conclusions, they show the expected dependence on topography and reasonable agreement with results of other methods (Bauer and Vaccaro, 1990).

Figure 25 shows saturated hydraulic conductivity measurements on Palouse samples by the falling-head centrifuge method. These K_{sat} results suggest an upper limit for the sensitivity of the K(θ) measurements to compaction.

Results of θ(Ψ) measurements by the SPOC method on core samples from the Idaho National Engineering Laboratory (Shakofsky and Nimmo, 1994; Shakofsky, 1995) appear in figure 26. These come from a study of the possible effects of structural differences between samples from an undisturbed soil and a simulated waste trench about 3 m away. This trench was constructed by back filling with soil that had been temporarily excavated. The most obvious difference is a substantially wider spread in characteristics among the undisturbed samples, indicating that the natural medium has layers with distinct hydraulic properties and that in the

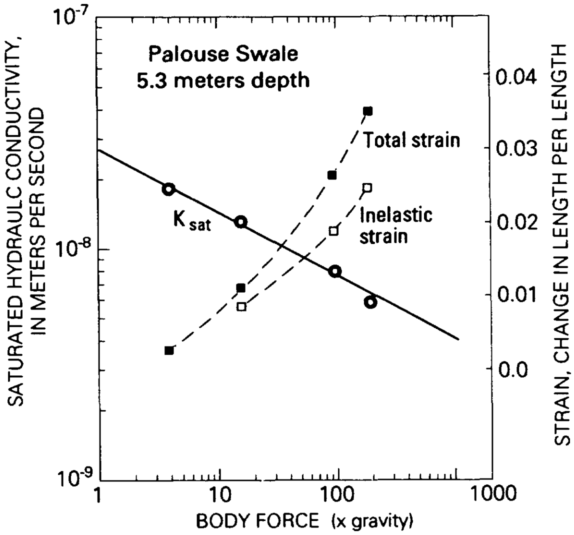

Figure 25. Falling-head centrifuge measurements of saturated hydraulic conductivity (K_{sat}), and compressive strain (fractional change in sample height L), as a function of the centrifugal body force. Results quantify the decline in K_{sat} with the increase in total compressive strain, measured during centrifugation with a linear displacement transducer. The inelastic component of strain was measured after centrifugation ceased. The in situ overburden pressure at the 5.3-meter depth of this sample corresponds to a body force of about 130 g.

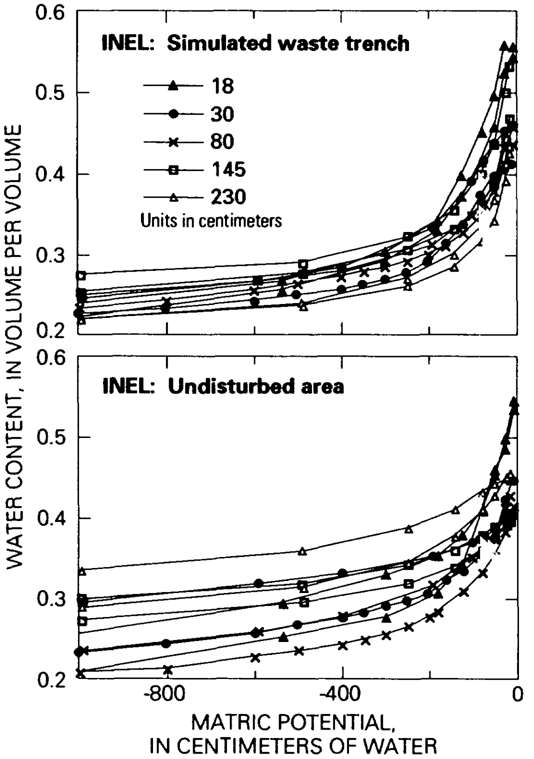

Figure 26. Moisture retention drying curves for samples from five depths in a simulated waste pit at the Idaho National Engineering Laboratory (INEL) and from the same depths in the adjacent undisturbed area.

simulated waste trench these layers are to some degree homogenized. The absence of natural layering may substantially influence water movement, affecting the wetness of soil near the buried waste as well as the recharge flux. In general the vertical movement of water would be expected to be retarded in a more distinctly layered system, suggesting that the construction of the waste trench disrupted some of the natural inhibitions to downward flow.

Measurement techniques are available for all of the properties needed for unsaturated flow determination, though requiring varying degrees of effort. In particular, the unsaturated K is indispensable in computing flow rates but measuring it accurately involves at least moderate difficulty. Commonly used techniques for determining K from easier types of measurements have accuracy that is far from adequate for a useful determination of the most critical unsaturated zone fluxes. Important directions for future research are to test the SSCM with a wider variety of media, to reduce the effort required for accurate $K(\theta)$ measurements, and to further develop unsaturated flow theory in ways that reduce the need for plentiful data.

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PROBLEMS OF FIELD IDENTIFICATION OF PREFERRENTIAL FLOW THROUGH FRACTURED MEDIA

By Edwin P. Weeks

Introduction

A major concern in low-level radioactive waste disposal is that of deep percolation through the waste repository. Traditionally, such deep percolation has been assumed to arise from diffuse, areally distributed infiltration that moves below the root zone and then to the water table. However, particularly in arid and semiarid regions, much of the recharge that occurs may result from the short-term penetration of water through distinct pathways that bypass most of the unsaturated zone volume. Such preferential flow is particularly common in fractured rock terrain, such as basalts at the Idaho National Engineering Laboratory (INEL), and welded tuffs at the Nevada Test Site (NTS).

Occasional localized recharge, although a potentially significant mechanism for radionuclide transport, is extremely difficult to quantify. Traditionally, estimates of local recharge have been based on such techniques as monitoring of the progression of wetting fronts by use of neutron logging, Darcy's Law-based estimates from measurements of hydraulic gradients and unsaturated hydraulic conductivity, estimates based on the chloride mass balance in water in the unsaturated zone, and methods based on determining the depth of penetration of tritium or other environmental tracers. These methods assume that recharge is areally distributed, and, for the chloride mass balance and environmental tracer techniques, that it occurs by piston displacement of the underlying unsaturated zone water. These assumptions are not met during recharge through preferred pathways, as much of the unsaturated zone water is bypassed.

Identification of Preferential Flow

Although not quantitative, one method to elucidate the dominant recharge mechanism is to compare the chemistry of deep unsaturated zone water or gas to that of ground water obtained from near the water table. If the ground water has the same chemical signature as the deep unsaturated zone water, either as measured or as inferred from the gas chemistry, recharge is likely diffuse and continuous. If instead, the ground water chemical signature resembles that of the atmosphere, one would suspect that ground water is dominantly recharged by flow through preferential pathways.

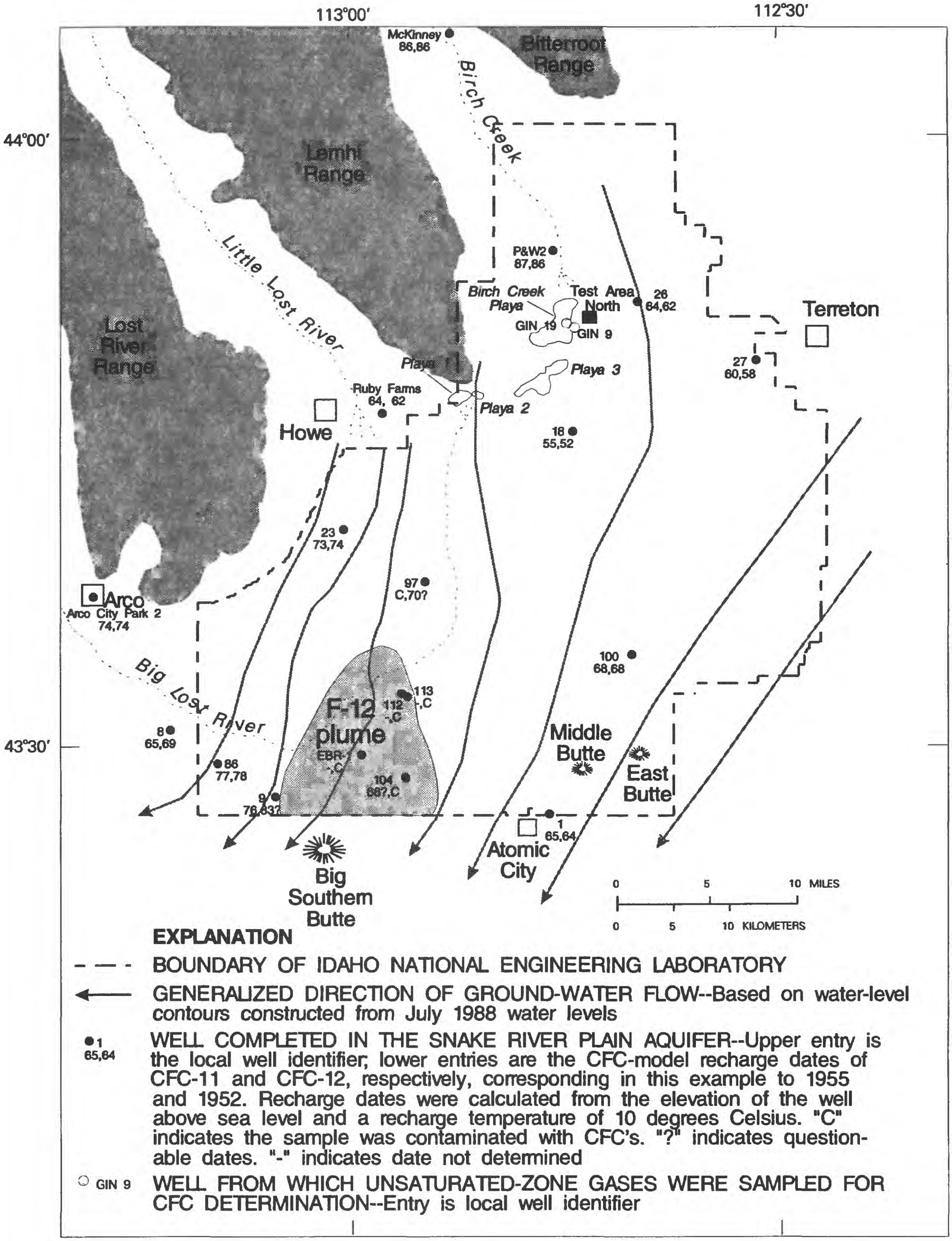
Two field examples illustrate the application of this approach. One involves the simultaneous sampling of chlorofluorocarbons (CFCs) in ground water and in gas from the deep unsaturated zone at INEL. The other involves comparison of the chemistry of water that collected in relatively shallow dry wells that terminate as open hole far above the water table at NTS, to that of ground water from deep wells that penetrate the water table and to that of unsaturated zone waters squeezed from cores.

INEL Study

The study at INEL is described in detail by Busenberg and others (1993). Briefly, waters were sampled from 24 wells, of which 12 were uncontaminated, for CFCs in and near INEL. Rock gas was also sampled for CFCs from various depths in the unsaturated zone at a piezometer installation in Birch Creek playa (fig. 27). The samples were taken from seven piezometers in two nests (GIN 9 and GIN 19) (Schmalz, 1969), that tap playa sediments and the underlying Snake River Plain basalts. At both nests, the playa sediments overlying the basalts are about 16 m thick, and the unsaturated basalts extend to the water table at a depth of about 62 m. Playas in the Snake River Plain represent terminuses of ephemeral streams arising in the adjacent mountains that periodically debouch onto the plain. Water collects in these playas following runoff events and either infiltrates the playa sediments or evaporates. In general, one would anticipate that distributed diffuse recharge would occur over the area of the playa.

Results of the rock gas sampling in terms of the concentrations of CFC-11 and CFC-12 with depth are shown in table 7. The concentrations decline rapidly with depth, and are relatively small just above the water table (57.6 m, GIN-19). A comparison of the concentrations at this depth to the historical buildup of CFCs in the atmosphere suggests that ground water having CFC concentrations in equilibrium with those measured in the gas at this depth would have an apparent CFC-11 date, based on the water having equilibrated with the atmosphere at that time, of 1963. The apparent CFC-12 date, on the other hand, would be 1971. These dates contrast with those determined by analyses of ground-water samples obtained from the nearby P&W2 well of 1987 for CFC-11 and 1986 for CFC-12 (table 8). These data suggest that slow uniform percolation through the unsaturated zone is not the dominant recharge mechanism in the vicinity of Birch Creek Playa.

Busenberg and others (1993) show that the rock-gas CFC profiles are quite plausibly explained by assuming gaseous diffusion as the dominant transport mechanism by which the CFCs reach depth in the unsaturated zone. Because of the larger gas diffusion coefficient and lower solubility in water of CFC-12 than of CFC-11, the apparent age of CFC-11 in the deep unsaturated zone should always be older than that of CFC-12 if diffuse, areally distributed recharge prevails. For deep unsaturated zones, on the order of tens to hundreds of meters thick, the apparent



EXPLANATION

- - - BOUNDARY OF IDAHO NATIONAL ENGINEERING LABORATORY

←— GENERALIZED DIRECTION OF GROUND-WATER FLOW--Based on water-level contours constructed from July 1988 water levels

●1 65,64 WELL COMPLETED IN THE SNAKE RIVER PLAIN AQUIFER--Upper entry is the local well identifier; lower entries are the CFC-model recharge dates of CFC-11 and CFC-12, respectively, corresponding in this example to 1955 and 1952. Recharge dates were calculated from the elevation of the well above sea level and a recharge temperature of 10 degrees Celsius. "C" indicates the sample was contaminated with CFC's. "?" indicates questionable dates. "-" indicates date not determined

○ GIN 9 WELL FROM WHICH UNSATURATED-ZONE GASES WERE SAMPLED FOR CFC DETERMINATION--Entry is local well identifier

Figure 27. Location of selected wells and piezometers, Idaho National Engineering Laboratory and vicinity

Table 7. Concentrations of chlorofluorocarbon-11 and chlorofluorocarbon-12 in the unsaturated zone at Birch Creek playa, Idaho National Engineering Laboratory, Idaho

[Concentrations are in pptv (parts per trillion by volume); ---, no data

Piezometer	Depth (meters)	CFC-11	CFC-12
GIN-19	3.0	279	492
GIN-19	31.7	116	269
GIN-19	41.1	80	207
Gin-19	57.6	19	137
Gin-9	3.0	275	492
GIN-9	16.5	131	305
GIN-9	24.4	157	274
Air	---	273	498

age discrepancy should be of a few to several years in magnitude. However, the ground water sampled in the vicinity of INEL (table 8) provided CFC-11 and CFC-12 ages that are nearly identical. These observations indicate that ground-water recharge throughout the INEL area occurs episodically as slugs of water that do not equilibrate with the soil-gas atmosphere at the base of the unsaturated zone.

Nevada Test Site Study

Another set of observations involving sequences of fractured welded tuffs interbedded with nonwelded tuffs at the NTS (fig. 28) also provides evidence suggesting that episodic water movement through preferential pathways may be the dominant recharge mechanism in many areas of the site. These observations include comparisons of water chemistry for residual moisture within the unsaturated zone, for water that collects in some shallow, normally dry wells immediately following precipitation events, and for ground water sampled in deep wells.

The dry wells were installed to allow access for neutron logging, which in turn was conducted to provide information on infiltration and deep percolation by monitoring the progression of wetting fronts moving through the unsaturated zone. During runoff from snowmelt or rainfall events, water apparently moves along fractures to these wells and collects in them at a typical depth of about 15 m. This accumulation occurs without any neutron-log based evidence of increased moisture content higher in the hole. The accumulated water typically has a tritium activity of about 25 tritium units (TU), which is very similar to that of simultaneously collected precipitation samples. Thus, the collected water appears to contain little residual unsaturated-zone water, and instead includes infiltrated water from recent precipitation that has bypassed the main volume of the unsaturated

Table 8. Chlorofluorocarbon-based dates of ground-water recharge for selected wells, Idaho National Engineering Laboratory and vicinity [CFC, Chlorofluorocarbon]

Well number	CFC-11 model age	CFC-12 model age
USG1	1964	1964
USG86	1977	1978
USGS8	1965	1978
Arco City Park # 2	1974	1974
USGS 23	1973	1974
Ruby Farms	1964	1962
McKinney	1986	1988
P&W2	1987	1986
USGS 26	1964	1962
USGS 18	1955	1952
USGS 27	1960	1958
USGS 100	1968	1968

zone. Analyses are available for four samples, including three from different events in one dry well, and one from a single event in another.

The water wells include a number of deep wells originally drilled as test wells, as well as two water-supply wells (U.S. Department of Energy, 1988). These wells are typically 1,000 to 2,000 m deep, and have depths to water from land surface of several hundred meters. Analyses of ground-water chemistry are available for 11 wells tapping tuffaceous units in the southwest quadrant of the Nevada Test Site.

Water samples from the unsaturated zone were obtained by squeezing cores obtained from three wells, including two drilled in the floor and flank of a wash, and one drilled on a ridge. Water samples were obtained from 47 cores for these analyses (Peters and others, 1992). The wells installed in and on the flank of the wash were installed with the concept in mind that diffuse recharge would be occurring beneath the wash, and that information could be obtained by contrasting measurements of moisture content, moisture tension, and of environmental tracer concentrations between the two wells. Instead, there was no noticeable difference in the overall distribution of chemical constituents between the sites.

Median or mean major ion chemistry for water samples from the three sources are shown in table 9. Major ion chemistry for the dry-well water is quite similar to that of ground water. Water sampled from the residual moisture in the unsaturated zone by core squeezing, on the other hand, is substantially more concentrated, for all ranges of pressure extraction, in most of the major ions than

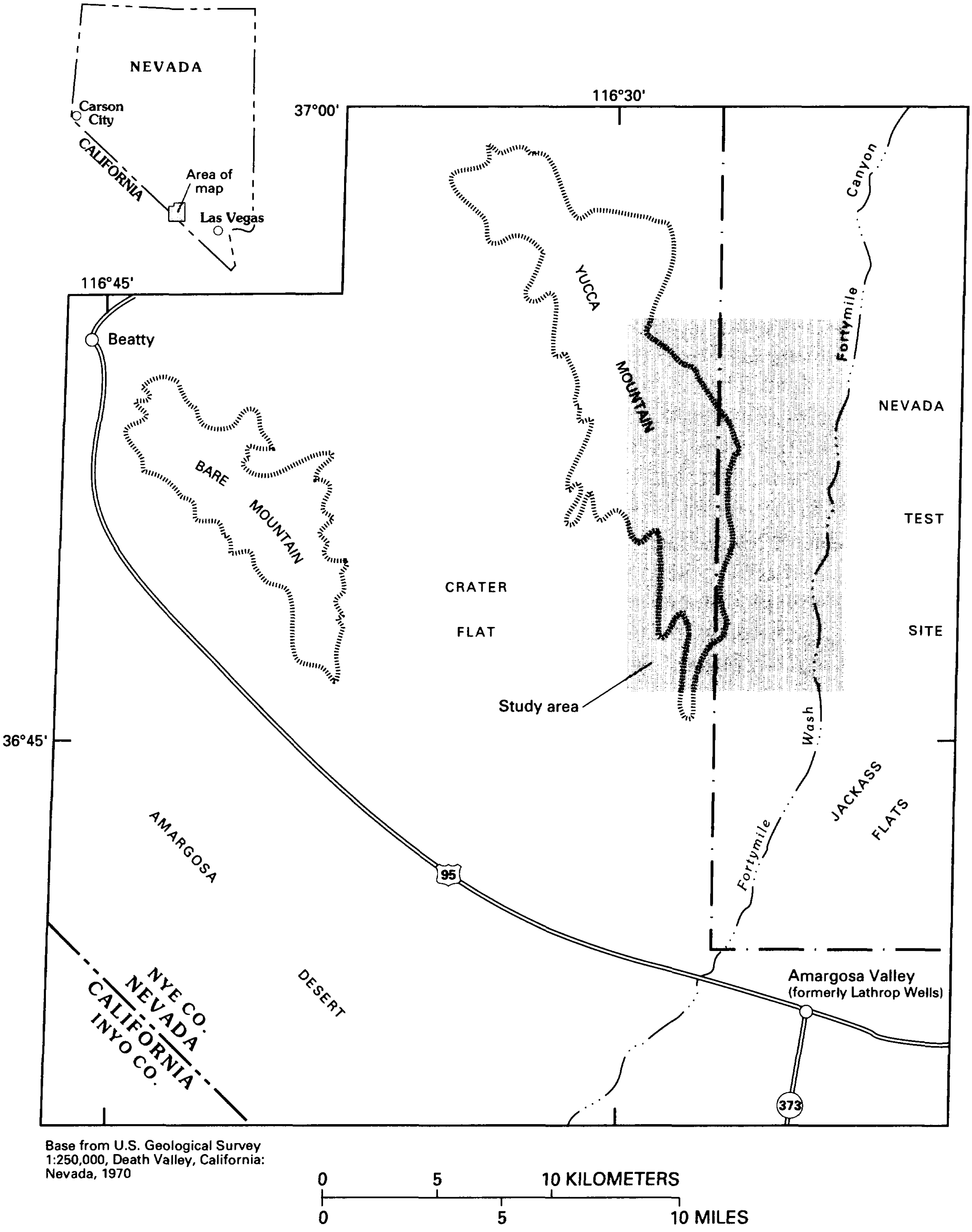


Figure 28. General location of ground water, ephemeral dry-well water, and unsaturated zone residual moisture sampling at the Nevada Test Site and vicinity.

Table 9. Major ion concentrations in ephemeral water from dry wells, ground water, and residual moisture from the deep unsaturated zone at the Nevada Test Site

Water source	Calcium	Magnesium	Sodium	Sulfate	Chloride	Alkalinity
Dry wells	0.7	0.2	0.8	0.7	0.2	0.3
Ground water	.6	.03	22	.4	.2	1.3
Residual moisture	4.6	1.5	1.8	2.5	4.0	1

either the deep ground water or the ephemeral dry-well water. These results suggest that ground-water recharge, if occurring at present, is very likely from occasional events that infiltrate through preferred pathways without interacting with the major portion of the unsaturated zone volume.

In conclusion, results of analyses of various chemical constituents in the unsaturated zone and the underlying ground water indicate that, even in the vicinity of washes or terminal discharge playas, most of the recharge appears to be derived from water that bypasses a major part of the unsaturated zone. If this is true, attempts to quantify local recharge using existing techniques may not be successful. A major research challenge for hydrologists will be to develop techniques that will be successful in these circumstances.

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ESTIMATING DEEP PERCOLATION OF PRECIPITATION AT THE U.S. DEPARTMENT OF ENERGY HANFORD SITE USING TWO CHLORIDE-TRACER METHODS

By Edmund A. Prych

Introduction

Radioactive materials have been processed, stored, used, or disposed of at the U.S. Department of Energy Hanford Site in arid south-central Washington since 1944 (fig. 29). Although precipitation averages only about 160 mm/yr, deep percolation of water from precipitation occurs. Therefore, quantifying the rates at which water percolates through soils and sediments to the water table is critical for assessing environmental risks posed by existing wastes, and for selecting isolation or treatment strategies for storage and remediation. Murphy and others (1991) reviewed previous investigations that used lysimetry, numerical modeling, and soil-moisture accounting to estimate deep percolation at Hanford. Most of these studies indicate that deep percolation is zero to a few millimeters per year where the surficial layer of soil is fine grained or is populated with deep-rooted plants. However, deep percolation can be a large fraction of annual precipitation where surficial soil is coarse grained and is without deep-rooted plants.

This paper summarizes the results of a study that used a chloride mass-balance and a ^{36}Cl bomb-pulse method for estimating deep-percolation rates at selected locations on the Hanford Site. These methods provide estimates that are independent of previous estimates and that are averages over long periods of time—about 35 yr for the bomb-pulse method, and thousands of years for the mass-balance method.

Methods

The ^{36}Cl bomb-pulse method for estimating deep percolation uses as a tracer the relatively large amount of ^{36}Cl that was introduced into the atmosphere by nuclear-bomb tests in the Pacific Ocean during the 1950's and that returned to the earth's surface as fallout (Phillips and others, 1988). The amount of water in the soil column above the level where ^{36}Cl concentrations are larger than natural is the amount of water that has infiltrated the ground since the bomb tests and has not yet been lost by evapotranspiration. Dividing this amount of water by the time since the tests provides an upper limit of the deep-percolation rate at a site. Actual deep-percolation may be less than this limit because some of the shallow soil water may be lost by evapotranspiration before it moves deeper. When using this method, one assumes that the bomb tests are the only anthropogenic sources of ^{36}Cl, that all chloride is dissolved in soil water, and that all water and chloride at the same depth move at the same rate (so-called piston flow).

Allison and Hughes (1978) demonstrated the use of a chloride mass-balance method for estimating local long-term deep-percolation rates. This method is based on the hypothesis that all or a known fraction of chloride in precipitation and dry deposition is transported in solution by water as it percolates to the water table. It is assumed that atmospheric deposition is the only source of chloride, and that water and chloride move as piston flow. As water percolates downward, chloride concentration increases when water is lost by evapotranspiration. Water that percolates to depths greater than that at which evapotranspiration occurs is termed deep percolation and will become ground-water

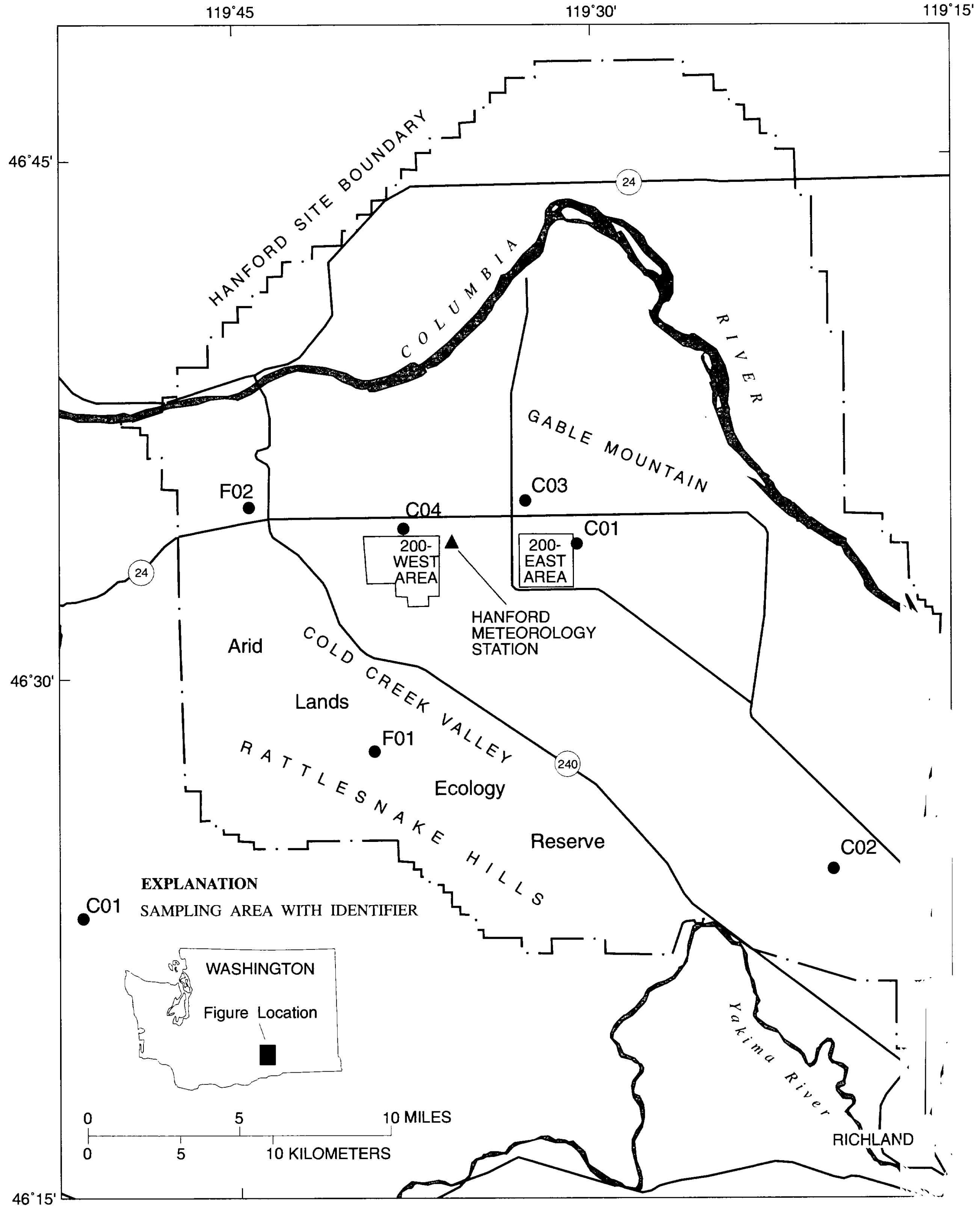

Figure 29. U.S. Department of Energy Hanford Site showing locations of sampling areas.

recharge when it reaches the water table. The rate of percolation, q_w, at any depth is estimated as:

$$q_w = q_{Cl}\,[Cl]_w \tag{2}$$

where q_{Cl} is the mass flux of chloride per unit horizontal area, which is assumed to equal the rate of atmospheric deposition, and $[Cl]_w$ is the observed chloride concentration in soil water. The flux, q_{Cl}, is calculated from the relation:

$$q_{Cl} = q_{^{36}Cl} / \left({}^{36}Cl/Cl\right) \tag{3}$$

where $q_{^{36}Cl}$ is the natural rate of production of ^{36}Cl in the atmosphere (about 22.5 atoms per square meter per second at the latitude of Hanford; Bentley and others, 1986), and ($^{36}Cl/Cl$) is the ratio of ^{36}Cl to total-Cl concentrations in deep soil water that is older than any anthropogenic ^{36}Cl. The average age of soil water or chloride at any depth can be estimated by dividing the amount of chloride above that depth by q_{Cl}.

Data for estimating percolation rates by the mass-balance method were obtained by collecting and analyzing soil samples from numerous depths down to 50 m in 13 test holes in 6 areas (fig. 29, table 10). All samples were analyzed to determine chloride content, water content and soil-moisture potential. Ratios of ($^{36}Cl/Cl$) were determined only in samples from 4 of the 13 test holes.

The soils on areas F01 and F02 consist of more than 4 m of silt loam. On areas C01, C03 and C04 the soils consist of about 0.6 m of loamy sand overlying tens of meters of glaciofluvial sand and gravel. Vegetation on these five areas consists of sage brush, other deep-rooted plants, plus sparse shallow-rooted grasses. Soils on the remaining area (C02) consist of 0.6 m of loamy sand overlying about 10 m of relatively clean sand. The only vegetation on this area is sparse shallow-rooted grasses.

Estimates of Deep-Percolation Rates

Upper limits of deep-percolation estimated using the ^{36}Cl bomb-pulse method range from 2.5 to 3.9 mm/yr at the three locations with sage brush (table 10). The depth of the centroid of ^{36}Cl from the bomb tests at these three locations ranged from 1.06 to 1.52 m (see table 10 and the example on fig. 30). The amount of bomb ^{36}Cl in the soil at these three locations (1.1 to 2.8×10^{12} atoms/m^2) is in the range found at arid sites in the southwest (see Phillips and others, 1988), which suggests that fallout of ^{36}Cl from operations at Hanford has been small compared with that from bomb tests. Data from hole B19 in the area with only grass are not yet complete; however, available data indicate that the centroid of bomb ^{36}Cl at B19 is deeper than 5 m, and that the estimated upper limit of deep percolation will be more than 8 mm/yr.

The atmospheric chloride flux that is estimated from (Cl^{36}/Cl) ratios ranges from 48 to 57 (mg/m^2)/yr. This is about three times as much as can be attributed to precipitation alone; consequently, dry deposition must account for about two-thirds of the total chloride flux.

Deep-percolation rates estimated by the chloride mass-balance method at nine locations with sagebrush range from 0.011 to 0.44 mm/yr (table 10). Estimated rates in the two areas with deep silt loam (F01 and F02) tend to be less than those in the other three areas (C01, C03 and C04). Estimated rates in the area with only sparse grass (C02) range from 0.48 to 2.4 mm/yr and are more than rates estimated in areas with sagebrush. Estimates by the mass-balance method are less than corresponding upper limits obtained by

Table 10. Estimated deep-percolation rates and related data

[^{36}CL, chloride-36; m, meter; atoms/m^2, atoms per square meter; mg/L, milligrams per liter; (mg/m^2)/yr, milligrams per square meter per year;
mm/yr, millimeters per year; ---, no data; <, less than, >, greater than; a, samples collected but data unavailable]

Sampling area and test-hole identifiers		Natural (CL^{36}/Cl) ratio [1]	Amount of bomb ^{36}Cl (atoms/m^2)	Depth to centroid of bomb ^{36}Cl (m)	Atmospheric Cl flux [(mg/m^2)/yr]	Chloride concentration [2] (mg/L)	Deep percolation by indicated method (mm/yr)	
Area	Hole						Mass balance	Bomb-pulse
F01	T01	---	---	---	57	3,100	0.018	---
F01	T02	735x10^{-15}	2.8x10^{12}	1.37	57	5,000	0.011	<3.9
F02	T03	854x10^{-15}	1.6x10^{12}	1.06	49	1,400	0.035	<2.5
F02	T04	---	---	---	49	320	0.15	---
C01	B10	---	---	---	48	760	0.063	---
C01	B12	---	---	---	48	1,600	0.030	---
C03	B17	---	---	---	48	520	0.092	---
C03	B18	---	---	---	48	110	0.44	---
C04	B20	876x10^{-15}	1.1x10^{12}	1.52	48	2,700	0.018	<2.8
C02	B14	---	---	---	48	100	0.48	---
C02	B15	---	---	---	48	20	2.4	---
C02	B16	---	---	---	48	35	1.4	---
C02	B19	a	a	>5	48	27	1.8	a

[1] Ratios determined by Dr. Pankaj Sharma and colleagues at Nuclear Structure Research Laboratory, University of Rochester.

[2] Used to estimate deep-percolation rate by mass-balance method

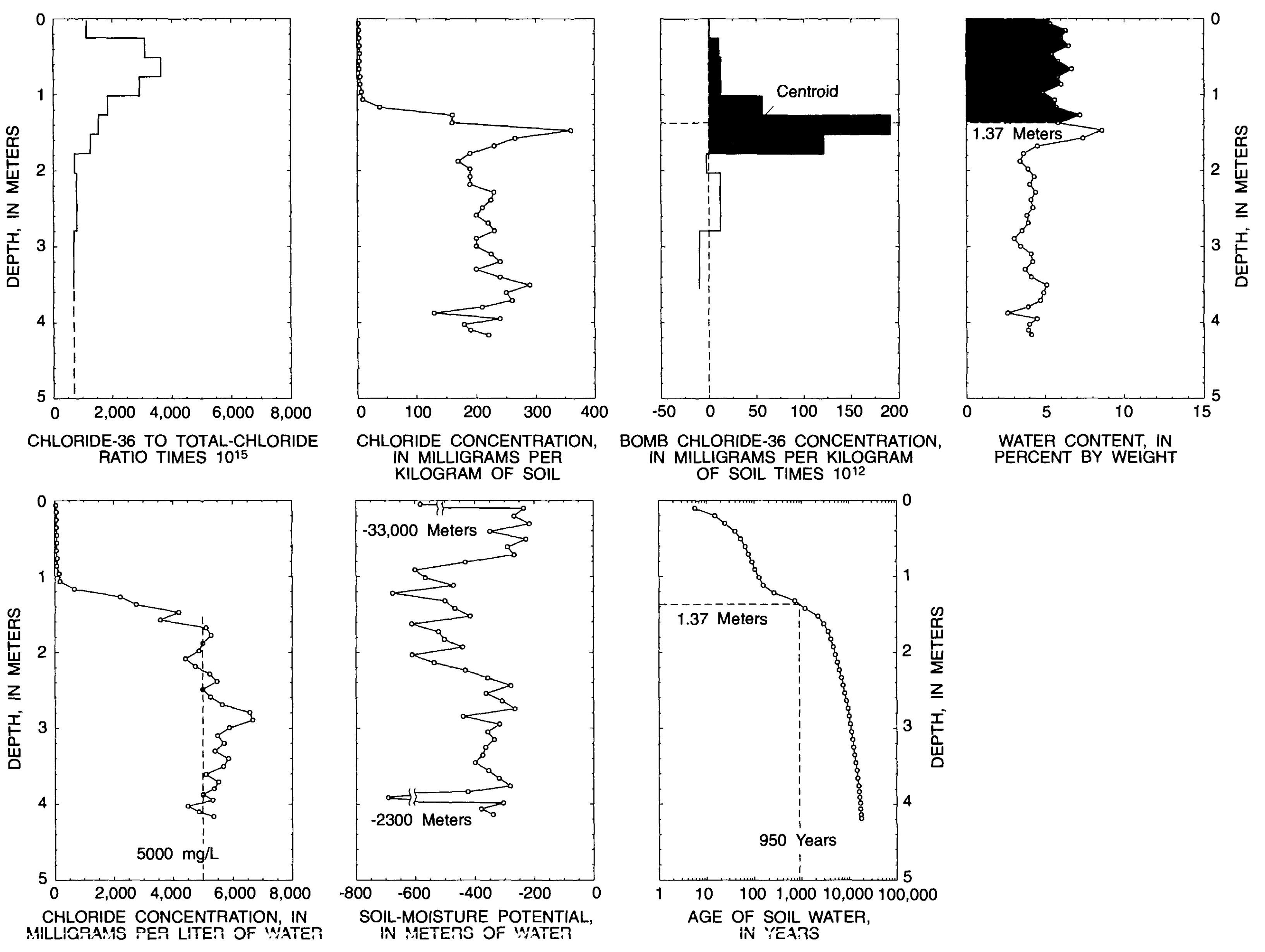

Figure 30. Vertical profiles of observed constituents and characteristics at hole T02 in sampling area F01.

the bomb-pulse method. Estimates in areas with sagebrush agree with estimates from previous studies that have used different methods; however, rates estimated in the area with only grass are at the lower end of the range of estimates from previous studies.

Although both chloride methods are based on the assumption that water and chloride move as piston flow, some data suggest that this assumption may not always be valid. For example, at hole T02 (table 10) the depth at which the ($Cl^{36}l/Cl$) ratio is a maximum is less than the depth to the centroid of bomb ^{36}Cl, and the age of soil water at the depth of the centroid (estimated by mass-balance calculations to be 950 yr) is much greater than the time since the bomb tests (33 yr). Similar differences exist in data from T03 and B20 (not shown). One of the mechanisms that could cause these differences is variations in the rate of movement of chloride within a given depth. These variations would have to occur over distances less than the horizontal dimensions of the soil samples (less than 0.3 m). Where these variations exist the mass-balance method would probably underestimate deep percolation. On the other hand, the bomb-pulse method would probably overestimate the upper limit, but the estimate would still be a valid upper limit. Although the magnitudes of the effects of variations in movement rate on the estimates are not known, the two estimates should bracket actual values.

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MEASURED AND PREDICTED WATER FLOW IN THE VADOSE ZONE AT THE HANFORD SITE

By G.W. Gee *and* M.J. Fayer

Introduction

Prediction of water flow in the vadose zone under arid-site conditions is an important and challenging problem. Decisions to bury radioactive wastes in arid environments may ultimately depend on how reliably we can predict water flow (as both liquid and vapor) in the vadose zone, since water is the dominant agent for carrying radionuclides and other contaminants from buried wastes through the vadose zone to underlying aquifers. While there have been significant advances in the past few years in modeling water movement in relatively dry soils, much less attention has been paid to obtaining detailed data sets to test these models, particularly for long-term predictions of water flow.

We have collected a series of multi-year data sets from the U.S. Department of Energy's Hanford Site, near Richland, Washington. These data document water flow in "dry" sediments, from near surface to depths as great as 18 m. Gravimetric sampling and neutron probe networks have been used to measure water storage in the top several meters of the soil profile for periods of a decade or more. In addition, precipitation, evapotranspiration, storage, and drainage have been monitored by use of lysimeters for over 20 yr. Within the past several years, improved data acquisition has allowed us to continuously monitor water movement in soils subjected to variable climate and surface wetness conditions. These data sets have been used to test transient water-flow models. We describe three sets of long-term data that have been used in model testing exercises. Limitations of model predictions are illustrated and recommendations are made for improvements in long-term modeling capabilities.

All tests were simulated using UNSAT-H (Fayer and others, 1992; Fayer and Jones 1990) a deterministic, one-dimensional, finite difference model based on the Richards equation. Inputs were daily weather records (precipitation, maximum and minimum temperature, humidity, wind speed, and solar radiation); average soil hydraulic properties (water retention and hydraulic conductivity); and when needed, plant transpiration algorithms (which empirically accounted for the dynamics of root growth and phenology).

Simulation 1

The first data set modeled was a 10-yr record of a 7.8-m deep, sand-filled lysimeter that was kept free of vegetation (Fayer and Gee 1992). Though the soil was initially "dry" (6 volume percent), water drained from this lysimeter after 3 yr. Model simulations underpredicted drainage and early spring water contents. An effort was made to optimize parameters and to include vapor flow in the simulations. When water vapor flow was included in the model and ten separate 1-yr simulations were run (using various combinations of selected hydraulic parameters) drainage was underpredicted by as much as 30 percent. In contrast, when vapor flow was not included, the drainage was overpredicted by as much as 165 percent. At present there appears to be no a priori way to estimate hydraulic parameters. This exercise illustrates how uncertainties in hydraulic parameters can affect drainage predictions for arid sites, particularly when simulations are extended for periods of a year or more.

Simulation 2

The second data set modeled was a 14-yr record of an 18-m deep, sand-filled lysimeter (Fayer and others, 1986; Gee and others, 1992; Gee and others, 1994). This is thought to be the longest record from the deepest lysimeter in the world. Neutron probe data were taken routinely for the first 7 yr and used to estimate water infiltration and drainage from this lysimeter. Initial reports on this lysimeter suggested that water movement at depth (below about 4 m) was negligibly low. In October 1985, nearly 14 yr after installation, the lysimeter was cored and sampled for water content. Water storage was found to have actually decreased (by more than 20 mm) from the initial water storage value. A model simulation of the deep lysimeter, using UNSAT-H, indicated that the only way that water storage could decrease over this time was to have water removal by vegetation. When vegetation growing on the lysimeter was simulated with an empirical algorithm that estimated the water removal by deep-rooted tumbleweed (a summer annual), there was good agreement between measured and predicted water storage. Routine neutron probe monitoring was discontinued for about 10 yr until February 1988, when all vegetation was removed from the lysimeter and periodic (bi-weekly or monthly) neutron probe monitoring was resumed. Data from the lysimeter and surrounding soils indicated that during a period of over 2 yr (February 1989 through March 1991), water storage in the lysimeter increased significantly compared to the adjacent vegetated soils, in qualitative agreement with UNSAT-H model predictions. Observations after March 1991 showed that the surface was revegetated by tumbleweed, so that all "excess" water in the top 5 m was removed by evapotranspiration in a matter of a few months (March through June). Removal of water via evapotranspiration also agrees with our model predictions.

Simulation 3

The final data set modeled was taken from two precision weighing lysimeters that have been used to measure changes in water balance under both irrigated and natural conditions (Fayer and others, 1992; Fayer 1993). The lysimeters are 1.5 m x 1.5 m in areal dimension and 1.7 m deep. The bottom of each lysimeter contains about 0.15 m of sand. The remainder is packed to a uniform density (1.4 g/cc) with Warden Silt Loam. The soil surface of each has been kept free of vegetation. Water storage changes (determined from lysimeter weight changes) were compared with model predictions over a period of two winters (18 months). Agreement between measured and modeled results compared well only after calibration of the model. Modifications of the hydraulic properties and estimated winter evaporation were required to obtain reasonable agreement in storage values for the 18-month period. When this calibration was used in simulating a 4.5-yr record, the predictions diverged from the measurements resulting in a significant underprediction (>50 mm) at the end of the test period for the irrigated lysimeter (total water application of 1,747 mm). Similarly poor agreement (an underprediction of nearly 50 mm) was obtained for the nonirrigated lysimeter (696 mm water) over the 4.5-yr test period.

Summary

In summary, models have been useful in providing qualitative performance of soils in limiting water infiltration and drainage at the Hanford Site. Significant drainage has been observed under arid-site conditions where soils are bare and coarse (for example, sandy textured, with water storage less than the annual precipitation). In contrast, finer soils drain only when water storage exceeds 500 mm (for example, more than three times the annual precipitation). Accuracy of predictions of drainage using the UNSAT-H model appears to be limited by uncertainties in hydraulic properties as well as estimates of winter evaporation. Further work is needed to test and calibrate UNSAT-H and other vadose-zone water flow models for long-term predictions at arid sites

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SIMULATED TRENCH STUDIES NEAR BEATTY, NEVADA—INITIAL RESULTS AND IMPLICATIONS

By B.J. Andraski

Introduction

In 1992, low-level radioactive wastes were disposed of by shallow-land burial at three commercial facilities in the United States: Barnwell, South Carolina; Beatty, Nevada; and Richland, Washington. The Beatty facility was closed in January 1993 and Barnwell is expected to close in July 1994. Several new facilities will be needed by the late 1990's. Near-surface disposal sites for low-level radioactive waste must be characterized, modeled, analyzed, and monitored (U.S. Nuclear Regulatory Commission, 1982, p. 57449). These USNRC regulations also require 1 yr of preoperational monitoring of a proposed site; the monitoring is limited to natural site conditions.

Sites in arid regions are considered ideal for waste isolation because potential evapotranspiration typically exceeds precipitation and ground-water recharge is assumed negligible. The numerous processes and interacting factors affecting water movement at arid sites, however, are not well understood (Andraski, 1992). The need to improve our understanding of these processes has been underscored by the current and proposed use of arid sites for disposal of several types of waste. Little comprehensive information about the natural soil-water flow systems at arid sites is currently available, however, and even less is known about how the natural site environment is altered by construction of a disposal facility.

The Beatty simulated-trench studies, which began in 1987, are designed to better define and evaluate the processes and interacting factors that can affect waste isolation. Objectives include: (1) determination of the effects of disturbance (trench construction and vegetation removal) on the natural soil-water regime and soil physical and hydraulic properties, (2) measurement of trench subsidence and erosion rates, and (3) evaluation and development of methods for reliable measurement of physical and hydraulic properties of dry soils. This paper presents results from the first 3 yr of a 5-yr field study to evaluate the effects of disturbance on the potential for deep percolation. The results are based on soil-water storage and water potential measurements in the upper 1.25 m during 1987-90.

Background of Beatty Site

Located in the Amargosa Desert of southern Nevada, the Beatty facility opened in 1962 and was the first commercially operated low-level radioactive waste facility in the United States. Based on disposal-facility records (R. Marchand, U.S. Ecology, Inc., unpub. data, 1991) and USGS data, annual precipitation during 1981 through 1990 averaged 104 mm and ranged from 14 mm (1989) to 225 mm (1983). About 70 percent of the precipitation falls during October through April, but snow is infrequent. Mean annual potential evaporation at Beatty, Nevada, is estimated to be about 1,900 mm (Nichols, 1987, p. 26). Daily mean air temperatures recorded at the site typically are highest during July, reaching as high as 38.6 C (Wood and others, 1992, p. 22). The facility is underlain by valley-fill deposits in which the depth to water ranges from 85 to 115 m below land surface (Fischer, 1992, p. 6). The alluvium-derived soils are horizontally stratified and the strata differ greatly in particle-size distribution and cohesiveness (Andraski, 1991). Vegetation is sparse and creosote bush (*Larrea tridentata*), an evergreen shrub, is the dominant species. The rooting depth of creosote bush closely corresponds with the depth of penetrating moisture (Wallace and Romney, 1972). Soil-water-monitoring and chloride data from the Beatty site indicate a rooting depth of about 0.75 to 1 m.

Detailed investigations at the Beatty site began in 1976 as part of the USGS program of research on low-level radioactive waste disposal. Through this program the USGS develops hydrogeologic information to assist Federal and State agencies and compacts of States in the development of disposal sites for low-level radioactive waste. Initial water-balance modeling for the Beatty site (Nichols, 1987) indicates that, under particular climatic and soil-moisture conditions, potential for deep percolation of water into the buried waste does exist, despite high annual evaporative demands. Subsequent studies, under undisturbed conditions include chloride-mass balance estimates of long-term recharge rates and field monitoring to characterize the natural soil-water regime. Fouty (1989) calculated long-term recharge rates, which ranged from 0.06 to 0.4 mm/yr, and suggested that drainage below the 10-m depth has been minimal or nonexistent for at least 6,000 yr. Fischer (1992) measured soil-water potentials at depths between 1 and 13 m, which ranged from -3 to -5.5 megapascals (MPa); below 9 m, potentials indicated a constant upward gradient. Both of these studies indicate that a natural system effectively limits the potential for deep percolation of infiltrated water. Little is known, however, about how, or to what degree, a natural site environment is altered by construction of a waste-disposal facility.

Field Experiment

Four treatments were evaluated adjacent to the burial facility: an undisturbed, vegetated soil profile; an undisturbed soil profile where vegetation was removed; and two unvegetated test trenches. The undisturbed site was established in 1983 (Fischer, 1992). The undisturbed soil and unvegetated trench sites (fig. 31) were established in September 1987 (Andraski, 1990). The small-scale test trenches were constructed to simulate those of the burial facility. The trench backfill and cover material is a homogeneous mixture of previously excavated soil.

Soil-water storage and potential were measured with a neutron probe and psychrometers, respectively. Storage measurements were made monthly and in response to precipitation. Concurrent storage monitoring of the test trenches and vegetated soil began in October 1987; continual monitoring of the unvegetated soil began in September 1988. The initial storage value for unvegetated soil was estimated from soil samples collected when vegetation was removed. Initial storage values (for 0- to 1.25-m depth) were 54 mm, vegetated soil; 51 mm, unvegetated soil; 56 mm, east trench; and 42 mm, west trench. Concurrent monitoring of daily soil-water potentials began in April 1988. Runoff was assumed negligible.

Initial Results of Investigation

Initial results from the simulated trench studies near Beatty, Nevada, demonstrate that the interactive effects of soils and vegetation are important in determining the soil-water balance and potential for deep percolation at an arid site. Disturbances caused by construction of burial trenches and removal of native vegetation have significantly altered the natural water balance. Precipitation and cumulative changes in soil-water storage greatly varied during the first year following trench construction (fig. 32). Total precipitation was 160 mm (154 percent of average), with

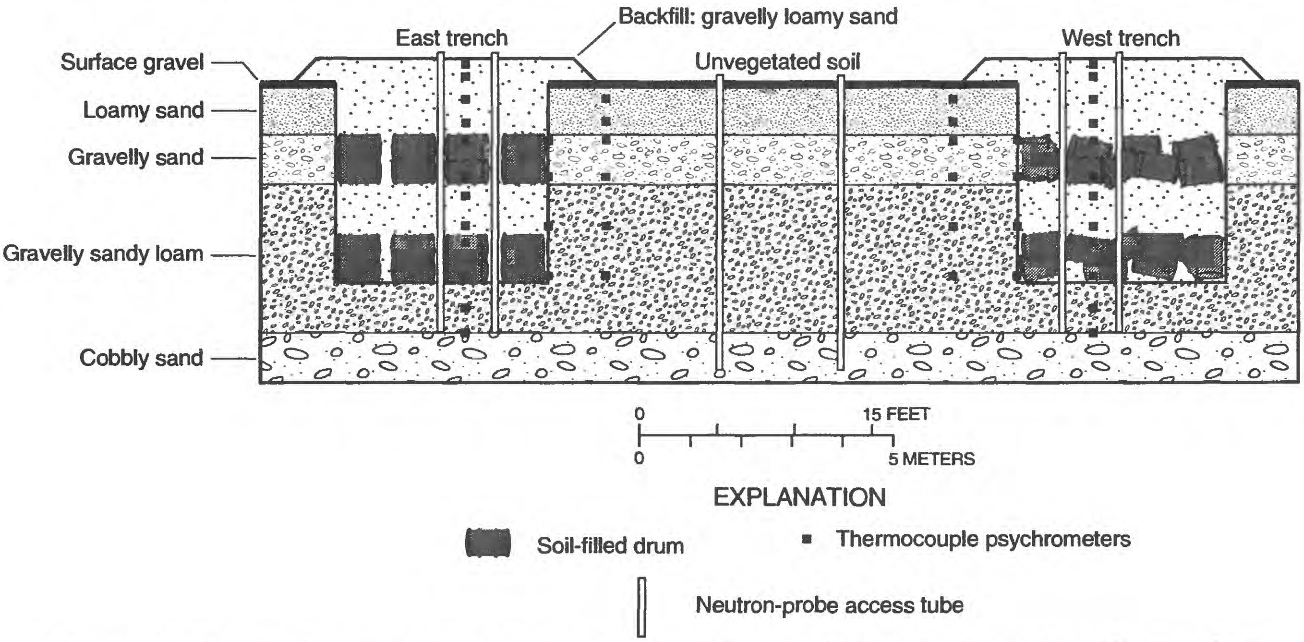

Figure 31. Schematic cross section showing instrumentation and lithology of unvegetated soil and test trenches.

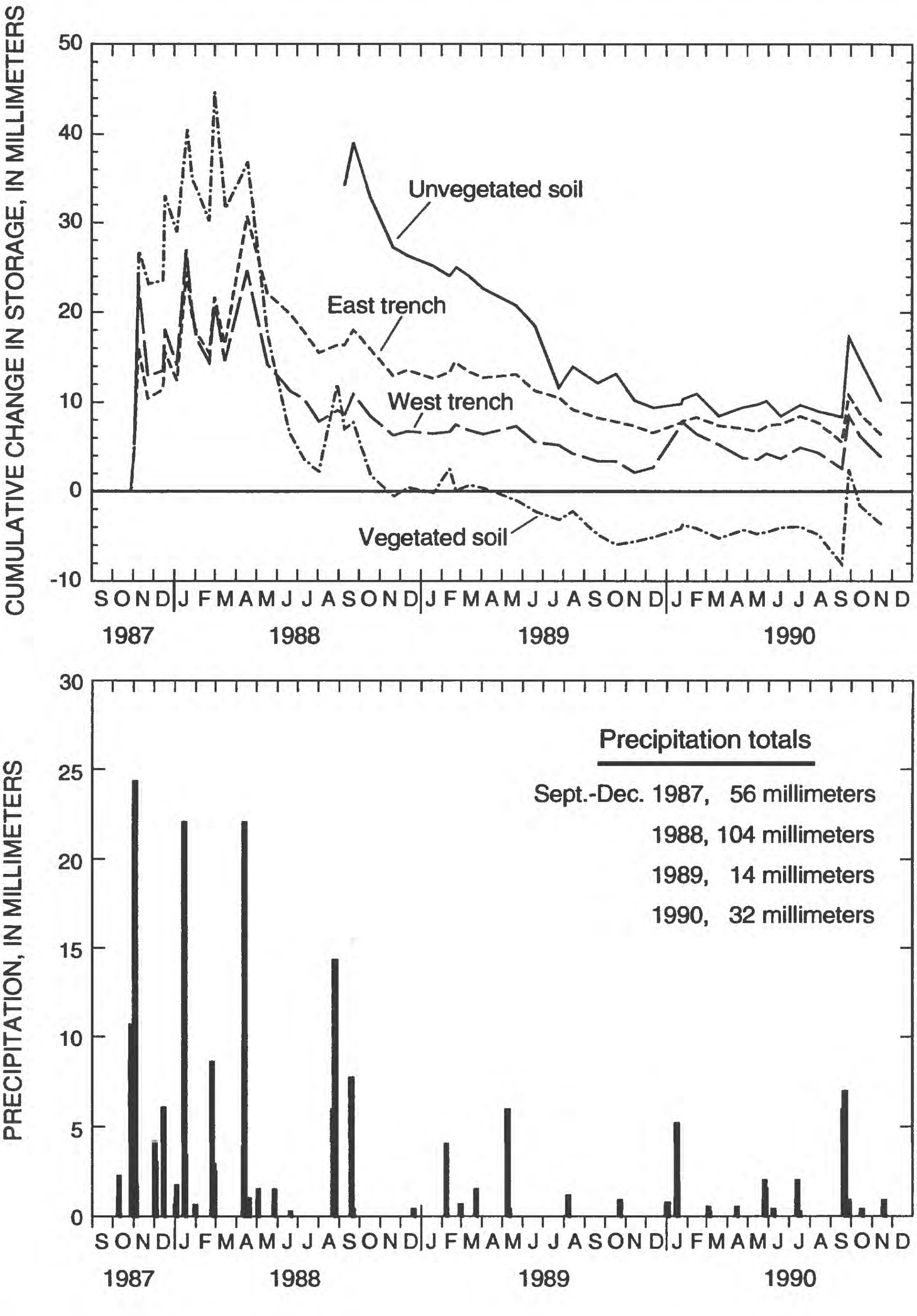

Figure 32. Daily precipitation and cumulative changes in soil-water storage (0- to 1.25-meter depth) relative to initial values for vegetated soil and unvegetated trenches (October 1987) and for unvegetated soil (September 1987). Continual monitoring of unvegetated soil began in September 1988.

100 mm measured by March 1988 (Wood and Fischer, 1992; Wood and others, 1992). Between October 1987 and March 1988, water depletion for vegetated soil was about 30 percent less than that for the east and west trenches. As a result, by March 1, 1988, the cumulative change in storage was greater for vegetated soil than for either of the trenches (fig. 33). Between March 1 and June 20, 1988, however, water depletion for vegetated soil was 109 and 73 percent greater than that for the east and west trenches, respectively. By June 20, 1988, cumulative change in storage was less for vegetated soil than for either of the trenches (fig. 33).

During March to June 20, 1988, depletion rates for vegetated soil averaged 0.6 mm/d compared to 0.3 mm/d for the east trench and 0.4 mm/d for the west trench. The average depletion rate observed for vegetated soil at the Beatty site during the spring was the same as that measured by lysimetry in a study of creosote bush near Tucson, Arizona (Sammis and Gay, 1979). In their 1-yr study, Sammis and Gay also compared depletion rates for vegetated and bare soil using neutron-probe data, but, in contrast to the Beatty findings and those from studies near Las

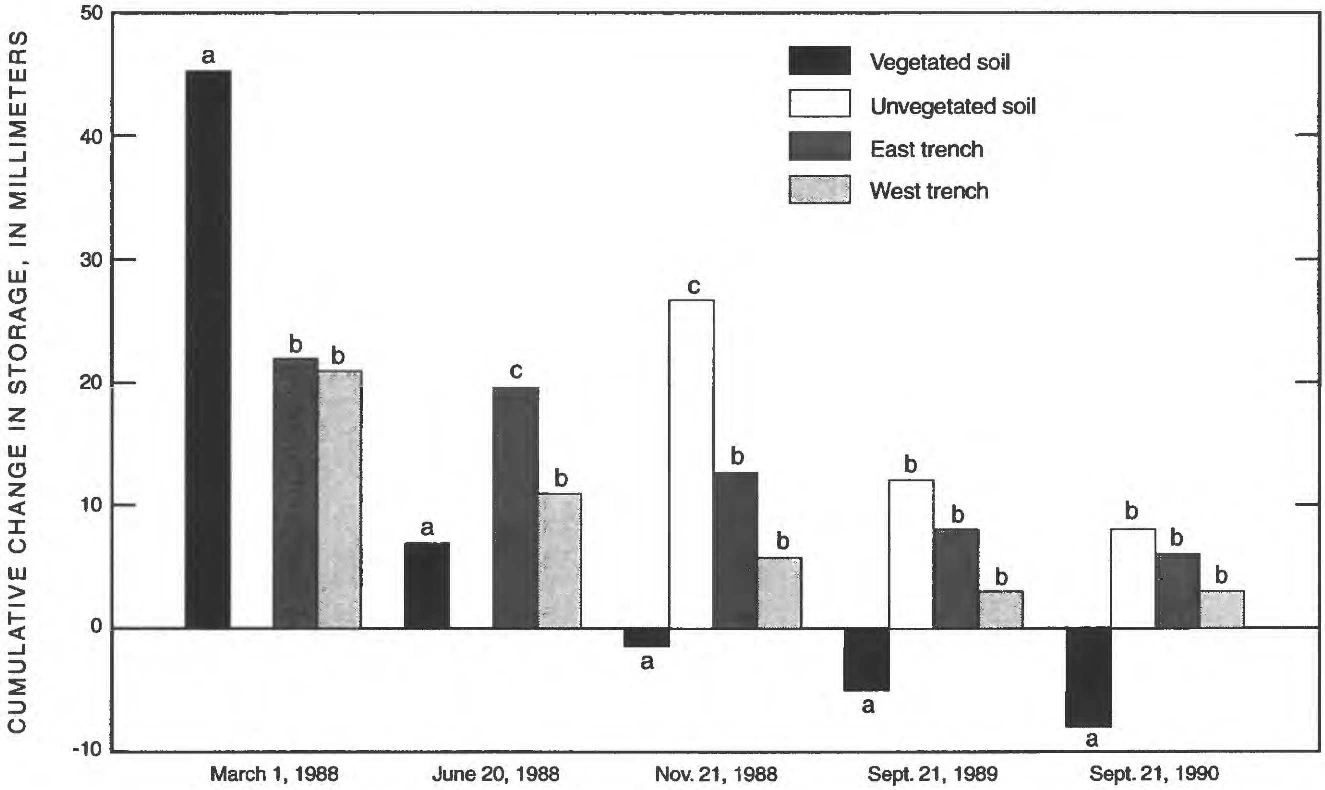

Figure 33. Cumulative change in soil-water storage (0 to 1.25-meter depth) for selected dates relative to initial values for vegetated soil and unvegetated trenches (October 1987) and for unvegetated soil (September 1987). Note: No measurements were made for unvegetated soil in March and June 1988. For each date, storage-change values labeled with same letter are not significantly different at 0.10 probability level as determined by Fischer's least-significant-different test (Steel and Torrie, 1980, p. 176); storage-change values labeled with different letters are significantly different.

Cruces, New Mexico (Gee and others, 1994), little difference was observed between vegetated and unvegetated soil at the Arizona site.

By November 21, 1988 (soon after the "wet" period), cumulative change in storage for vegetated soil decreased to -1 mm. This value was significantly less than storage values observed for each of the three disturbed sites (fig. 33).

Precipitation decreased to 14 mm in 1989 and was 32 mm in 1990, resulting in further decreases in soil-water storage (fig. 32). Even after these two extremely dry years, however, cumulative changes in storage for the disturbed sites remained high and values were significantly greater than those for vegetated soil (fig. 33).

The greater increases in storage often observed for vegetated and unvegetated soil immediately following precipitation are due to the natural structure of the undisturbed soil, which result in more rapid percolation and concomitantly smaller evaporative losses from near-surface soil. Soil-water potential data from depths of 0.6 m (vegetated soil) and 0.75 m (unvegetated soil and trenches) illustrate some of the differences in the rates and depths of percolation among the four treatments (fig. 34). Rapid percolation for undisturbed soil resulted in high soil-water potentials during spring 1988; potentials for the east trench show the wetting front did not reach the 0.75-m depth until June 1988; and potentials for the west trench show the wet-

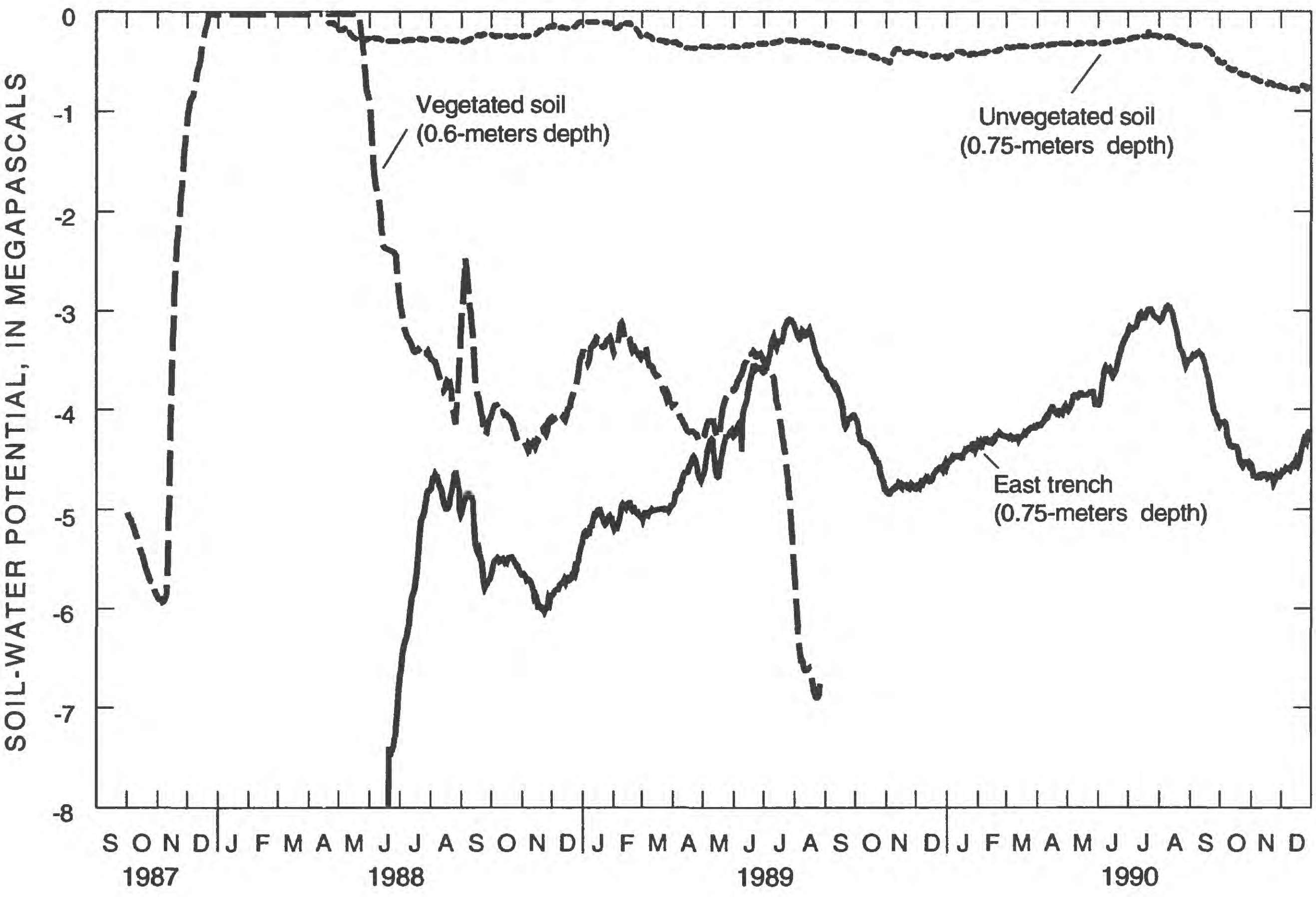

Figure 34. Daily soil-water potentials at 0.6-meter depth for vegetated soil and 0.75-meter depth for unvegetated soil and unvegetated east trench during 1988-90. Water potentials for west trench (0.75-meter depth) remained less than -8 megapascals.

ting front did not reach the 0.75-m depth during 1988-90. Differences between the trenches were due to the greater quantity of rock fragments at the surface of the east trench (0.45 kg/kg) in comparison with the west trench (0.23 kg/kg), which retarded evaporation and enhanced internal drainage. For undisturbed soil, although water potentials were relatively high during the spring of 1988, the textural change from gravelly loamy sand to gravelly sand at about 0.75 to 1 m deep, impeded continued downward percolation. (During 1988-90 water potentials for unvegetated soil at the 1.85-m depth varied seasonally from -2.5 to -7 MPa.)

Vegetation had a substantial effect on depletion of water accumulated in the root zone. Soil-water potentials for vegetated soil showed large decreases during 1988 and 1989 (fig. 34); the timing of these decreases closely corresponded with decreases measured for soil-water storage (fig. 32). In contrast, for both the unvegetated soil and the east trench, the range of soil-water potentials at the 0.75-m depth during the first year of the study generally persisted through 1990.

Application To Arid-Site Waste Disposal

The near-surface properties of undisturbed soil result in more rapid percolation and smaller evaporative losses than observed for the trenches. The stratified alluvial soil impeded the continued downward flow of water and where plants were present, accumulated water was rapidly depleted. In the absence of vegetation, water storage values for undisturbed soil and trench backfill remained elevated, thereby increasing the quantity of water available for deep percolation. Unlike the natural soil profile, however, the homogeneous trench backfill provides no stratification to impede continued downward flow of water.

The results presented in this paper also illustrate the episodic precipitation patterns common to arid regions and show the importance of multiple-year studies for evaluating the processes and factors controlling water movement at arid sites. The magnitudes of the soil and vegetation effects were observed to vary greatly in response to seasonal and annual climatic changes. Even under conditions of extreme aridity (206 mm of precipitation in 3.3 yr), however, the effects of disturbance on the soil-water balance remained evident.

The interactive effects of climate, soils, and vegetation are important in determining the soil-water balance and potential for deep percolation at an arid site. Disturbances caused by construction of burial trenches and removal of native vegetation can markedly alter the natural water balance. Consideration of such alterations is necessary in the siting and design of disposal systems and also in predicting the effectiveness of proposed sites and facilities for long-term waste isolation.

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A FIELD STUDY FOR EVALUATING UNSATURATED ZONE FLOW AND TRANSPORT MODELS

By P.J. Wierenga, R.G. Hills,
M.H. Young *and* J. Vinson

Introduction

Prediction of water flow and chemical transport from disposal areas generally requires the use of computer models. Numerical models have been developed for predicting water flow and solute transport in saturated or unsaturated soil systems. Due to the lack of sufficient field data, the validity of these models, especially as applied to dry soils on the field scale, has not been tested adequately. During the past 15 years, stochastic models for the prediction of water flow and chemical transport have received much interest (Russo and Bresler, 1981; Dagan and Bresler, 1979; Mantoglou and Gelhar, 1987). This interest resulted from the extensive variability in soil physical properties observed in the field. Unfortunately, in order to use stochastic models, statistical information on the hydraulic properties, such as the mean, variance, and correlation length, is required. Few data sets are available which include information on the statistical distribution and spatial dependence of the important hydraulic properties.

The Las Cruces Trench study was designed to develop a data base for testing deterministic and stochastic flow and transport models. A detailed field experiment was designed, in cooperation with Dr. Lynn Gelhar, Massachusetts Institute of Technology, and Dr. Glendon Gee, Battelle Pacific Northwest Laboratories, to study the movement of water containing a chemical tracer through an initially dry, spatially variable soil. Efforts were made to characterize the soil at the experimental site in sufficient detail so that deterministic and stochastic models for the hydraulic properties could be estimated.

In this paper, we provide an introduction to the characterization efforts and to the three experiments conducted at the site. The experimental methods used to characterize and monitor the site are described, and some of the experimental results on water flow obtained during the early phases of the dynamic experiment will be presented. A comparison of several models applied to the data is presented by Hills and Wierenga (these proceedings) in the paper following this presentation.

Methods and Materials

Site Description and Characterization

Much of the information in this report can be found in previously published reports and journal articles (Wierenga and others, 1989; Wierenga and others, 1990; Wierenga and others, 1991; Hills and others, 1991). A summary of this information is given below.

The experimental site is located on the New Mexico State University College Ranch, about 40 kilometers northwest of Las Cruces, New Mexico. The site is on a basin slope of Mount Summerford at the north end of the Dona Aña Mountains. The Dona Aña Mountains form a domal uplift complex of younger rhyolitic and older andesitic volcanics intruded by monzonite. Climate in the region is characterized by abundant sunshine, low relative humidity and an average Class A pan evaporation of 239 cm/yr. Average annual precipitation is 23 cm.

A 26.4 m long by 4.8 m wide by 6.0 m deep trench was constructed in the undisturbed soil to provide horizontal access to an irrigated plot and to provide soil samples. A 4 m by 9 m area was selected on the south side of the trench (fig. 35) for controlled application of water containing a tracer. After excavation of the trench, nine soil layers were identified based on the observed morphological horizons on the west wall of the trench and on the hydraulic properties of each layer.

The average bulk density for the nine layers ranges from 1.66 to 1.74 g/cm^3. Average $CaCO_3$ content ranges from 1.4 percent in the top layer to 22.6 percent in the eighth layer. The average coarse fraction ranges from 19.5 percent in layer 3 to 34.6 percent in layer 9. The results of the particle size analysis of the 50 soil samples taken from each layer indicate that the soils are sands, sandy loams, loamy sands, and sandy clay loams. Layers 2, 3, 4, 6, 8, and 9 show evidence of carbonate accumulation. There are various buried channels visible along the trench walls. The soil in these buried channels (arroyos) have no structure and the texture is gravelly sandy loam.

During construction of the trench, a total of 50 undisturbed core samples and 50 disturbed soil samples were collected from each of the 9 layers. The samples were collected along the north wall of the trench at 0.5 m intervals (in the horizontal direction). The sampling depths for the center of the soil core samples were 0.11, 0.71, 1.51, 2.16, 2.70, 3.20, 3.98, 4.89, and 5.79 m. The undisturbed soil core samples were collected in 7.6 cm inside diameter by 7.6 cm long aluminum rings. Each disturbed soil sample consisted of approximately 425 g of loose soil. Cores and disturbed soil samples also were collected

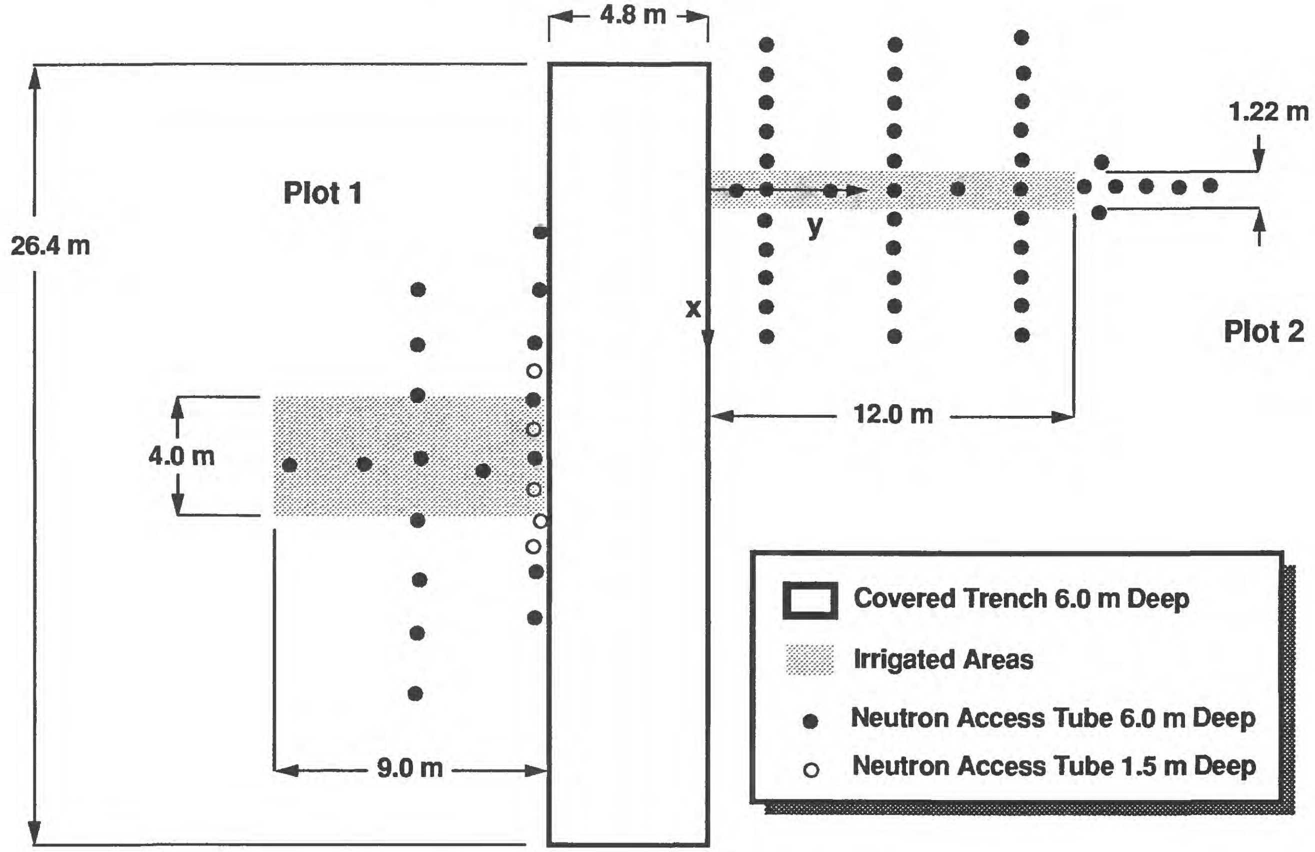

Figure 35. Overview of trench with locations of plots 1 and 2.

at approximately 13 cm depth intervals to a depth of 6.1 m in the vertical direction at three locations along the length of the trench. Altogether, a total of 594 soil cores and 594 disturbed soil samples were taken to the laboratory for the estimation of their bulk density, saturated hydraulic conductivity and the soil-water retention curve.

The saturated hydraulic conductivity of the soil was determined in situ with the Guelph permeameter method (Reynolds and Elrick, 1985). Holes 10 cm diameter by 15 cm deep were drilled in the undisturbed soil 30 cm to the side of each location where core samples were collected (50 per soil layer spaced 0.5 m apart for each of the 9 soil layers) along the north trench wall. Using the Guelph permeameter, a constant water level was maintained in each hole and the rate of flow into each hole was measured. The results from these measurements are presented in Wierenga and others (1989) and discussed by Nicholson and others (1987).

The saturated hydraulic conductivity of each core also was measured by applying a constant head differential across the cores and measuring the outflow using the method of Elrick and others (1980). The wet range of the soil water retention curves was determined by placing the saturated cores from each location into pressure boxes, subjecting them to differential pressures of 10, 20, 40, 80, 120, 200, and 300 mbar, and measuring the total outflow at each differential pressure. Once outflow ceased at 300 mbar pressure, the cores were oven dried at 105 °C for at least 7 days and the bulk density and water contents determined. The disturbed soil samples from each location were sieved and air-dried and used with a standard pressure plate apparatus (Soil Moisture Equipment Co., Santa Barbara, California) to determine soil-water retention data in the 1 to 15 bar (dry) range. The water retention data were fit to van Genuchten's water-retention model for each core location. This model for water retention is given by (van Genuchten, 1980).

$$S_e = \frac{\Theta - \Theta_r}{\Theta_s - \Theta_r} = \frac{1}{[1 + (\alpha h)^n]^m} \qquad (4)$$

$$m = 1 - \frac{1}{n} \qquad (5)$$

where Θ, Θ_r , and Θ_s are the volumetric water content, residual water content, and saturated water content, respectively; h is tension, α and n are the parameters to be estimated. Θ_r was set to the measured 15 bar water content value **and Θ_s was set to the gravimetrically measured value for each sample location. Given estimate**s of the parameters in equation (1) and laboratory estimates of the saturated hydraulic conductivity, K_s, at each location, Mualem's model (Mualem, 1976), as simplified by van Genuchten (1980), was used to predict the unsaturated hydraulic conductivity as a function of water content for each location.

$$K = K_s S_e^{\frac{1}{2}} \left[1 - \left(1 - S_e^{\frac{1}{m}} \right)^m \right]^2 \qquad (6)$$

Three infiltration experiments were conducted at the site. Experiment 1 was conducted on the south side of the trench, while experiments 2 and 2b were conducted on the north side of the trench (fig. 34). Water from a nearby well was applied through a closely spaced grid of drip emitters (approximately 0.30 m x 0.15 m) connected to header pipes, and a precisely regulated water-supply system. The amount of water applied was measured with flow meters, and also volumetrically. During tracer application, the water-supply system was connected to a tank holding well water spiked with the tracer. Visual inspection of the drip system showed no sur-

Table 11. Experimental conditions

[cm, centimeters; m, meters]

	Surface area m x m	Flux cm/day	Duration days	Tracers ---
Experiment 1	4.0 x 9.0	1.82	86.0	^{3}H,
Experiment 2	1.2 x 12.0	0.43	75.5	^{3}H, Br
Experiment 2b	1.2 x 12.0	1.82	70.0	^{3}H, Br$^-$, Cr, B, PFBA, DFBA

face ponding during water application. The irrigated and surrounding areas were covered by a pond liner to inhibit evaporation from the surface and to prevent infiltration of rainwater.

Neutron probes and tensiometers were used to measure water contents and tensions. Neutron probe access tubes were installed vertically down to a maximum depth of 6 m (fig. 35). The water contents of the soil removed during probe installation were measured gravimetrically, and their values used for probe calibration.

Tensiometers were installed through the trench face such that the porous cup of each tensiometer was inserted 50 cm, with an incline of 10 degrees from the horizontal, into the formation. The locations of the tensiometers used in experiment 2 are shown in figure 36. Tensions were measured daily through a septum stopper at the exposed end of each tensiometer with a hand held pressure transducer (Soil Measurement Systems, 7344 N. Oracle Road, Suite 170, Tucson, Arizona), after the wetting front had reached the tensiometer. Earlier readings have been unreliable due to the very dry initial conditions and the associated high tensions.

Soil solution samplers also were installed in a grid pattern through the trench wall in the same manner as the tensiometers (fig. 36). Once the water front had reached the samplers, a constant vacuum of approximately 200 mbar was applied to the samplers to collect soil solution samples for laboratory analysis. Soil cores were collected in plot 2 before and after experiment 2b. The boreholes were drilled to the 6.3 m depth after infiltration experiment 2b, along two transects perpendicular to plot 2, 5 and 9 m, respectively, from the trench face.

Results and Discussion

Figure 37 is an example of the data obtained from experiment 1. This figure shows the advance of the wetting front during irrigation of the 4 m wide by 9 m deep plot. The advance of the wetting front could readily be observed on the trench wall from the change in soil color due to wetting of the initially dry soil. The data in this figure show a fairly symmetrical, nearly semi-circular infiltration front after 34 days of water application. On day 50, when the front reached the 5.3 m depth, horizontal spreading near the surface was 1 m to the right, and 0.75 m to the left of the irrigated area. The advance of the wetting front also was evident from neutron probe and tensiometer readings (Wierenga and others, 1991). A simple one-dimensional model compared measured and predicted advances of wetting fronts and showed that model predictions lagged behind

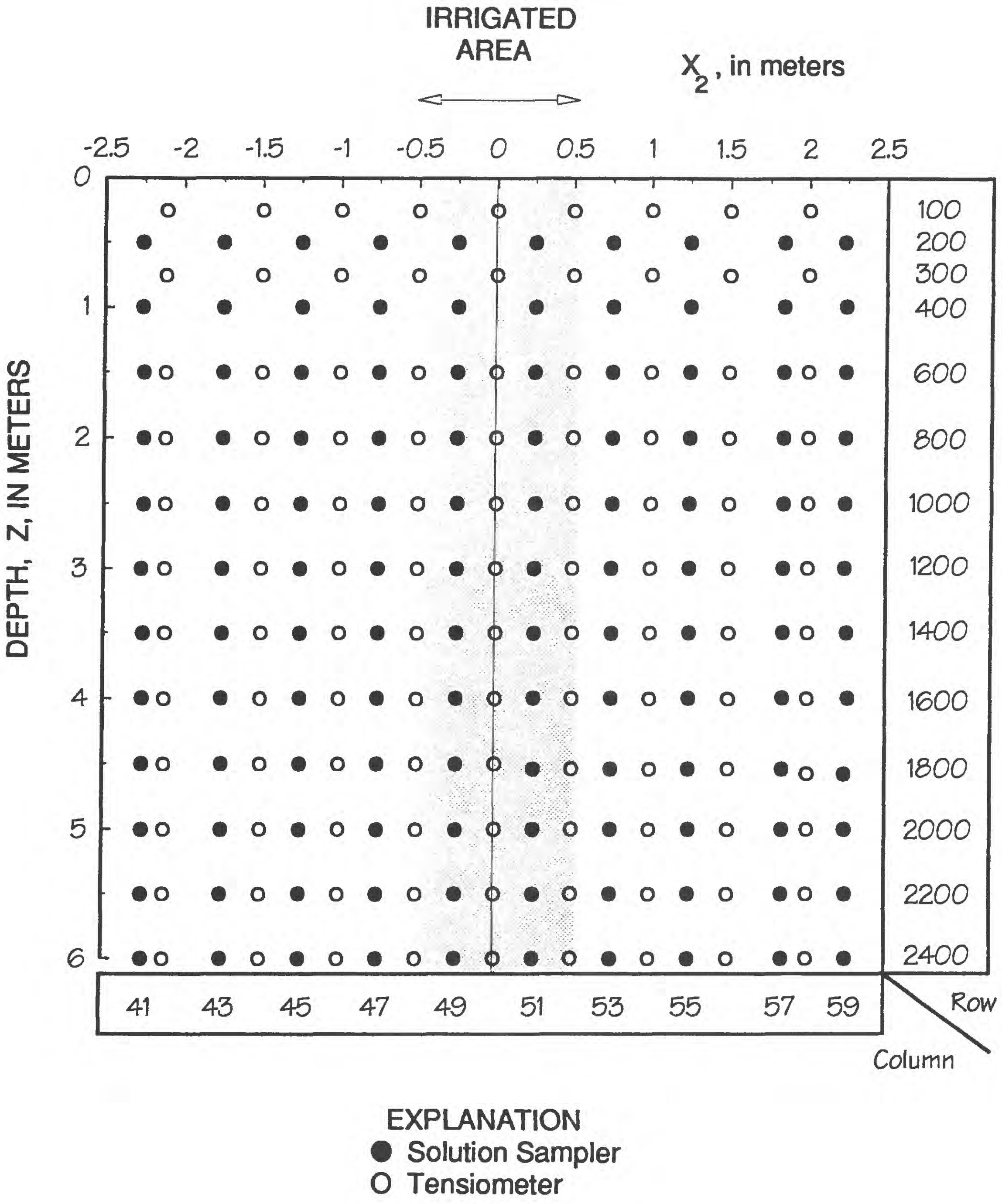

Figure 36. Location of solution samplers and tensiometers on trench wall of plot 2.

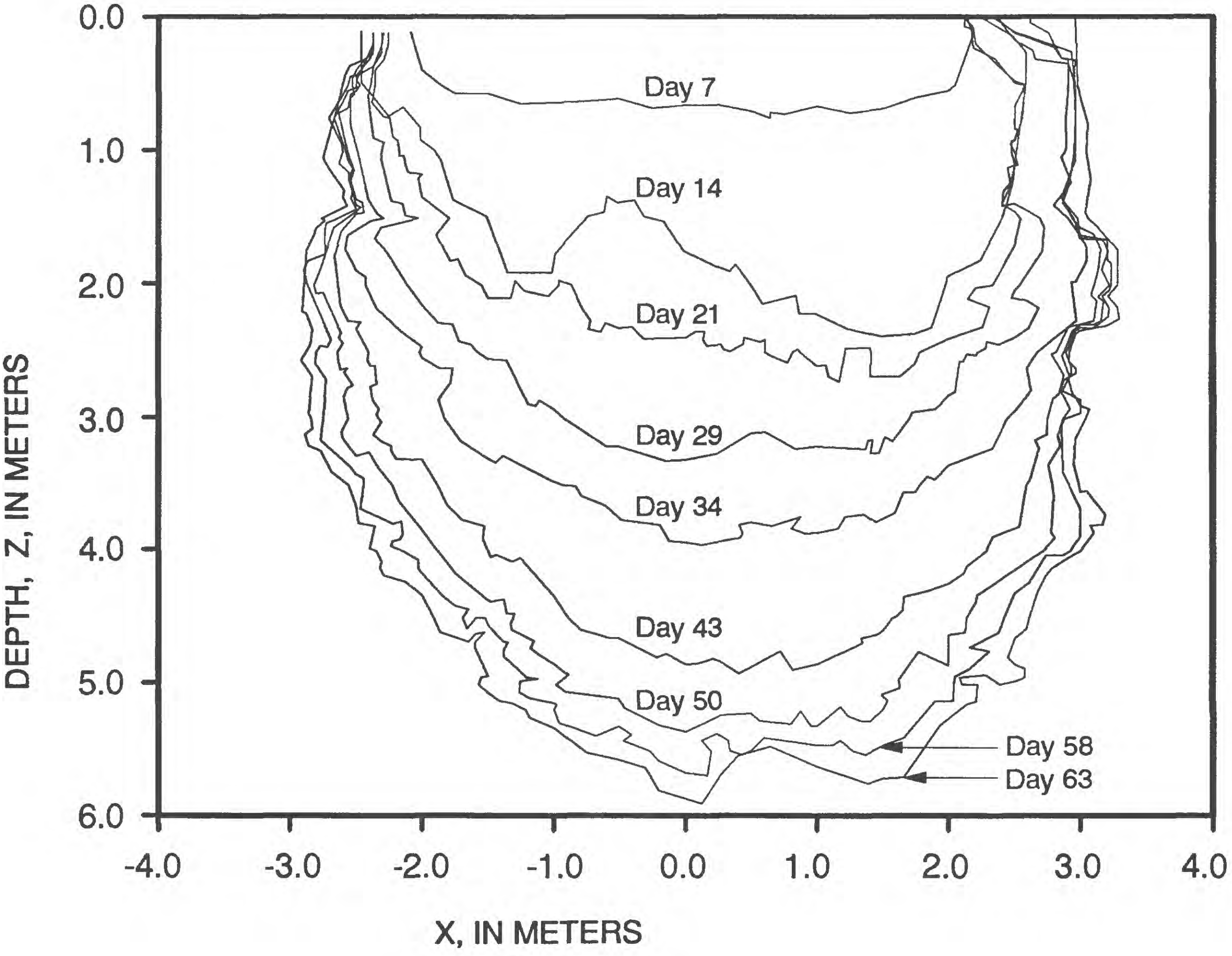

Figure 37. Advance of wetting front as observed on trench wall during irrigation of plot 1.

neutron probe measured fronts. However, predicted fronts tended to be ahead of those observed visually and inferred from the tensiometers.

Figures 38 and 39 show changes in water content on day 73 of experiment 2b. Figure 38 shows water content differences parallel to the trench face and perpendicular to the face at 2 m distance. Figure 39 also shows differences at 6 m and 10 m distances from the trench face. The differences in water content were obtained by subtracting initial water contents measured on day 0 from the water contents measured at each point on day 73. Unlike actual water content distributions, which are rather irregular due to the variability in water-retention properties across the measurement area (Hills and Wierenga, these proceedings), water content changes show a more consistent pattern. This is because water-retention curves for this soil have a similar shape, and thus addition of a given amount of water causes a similar increase in water content, even though the initial amount of water present may be quite different. The tracer distributions (not shown

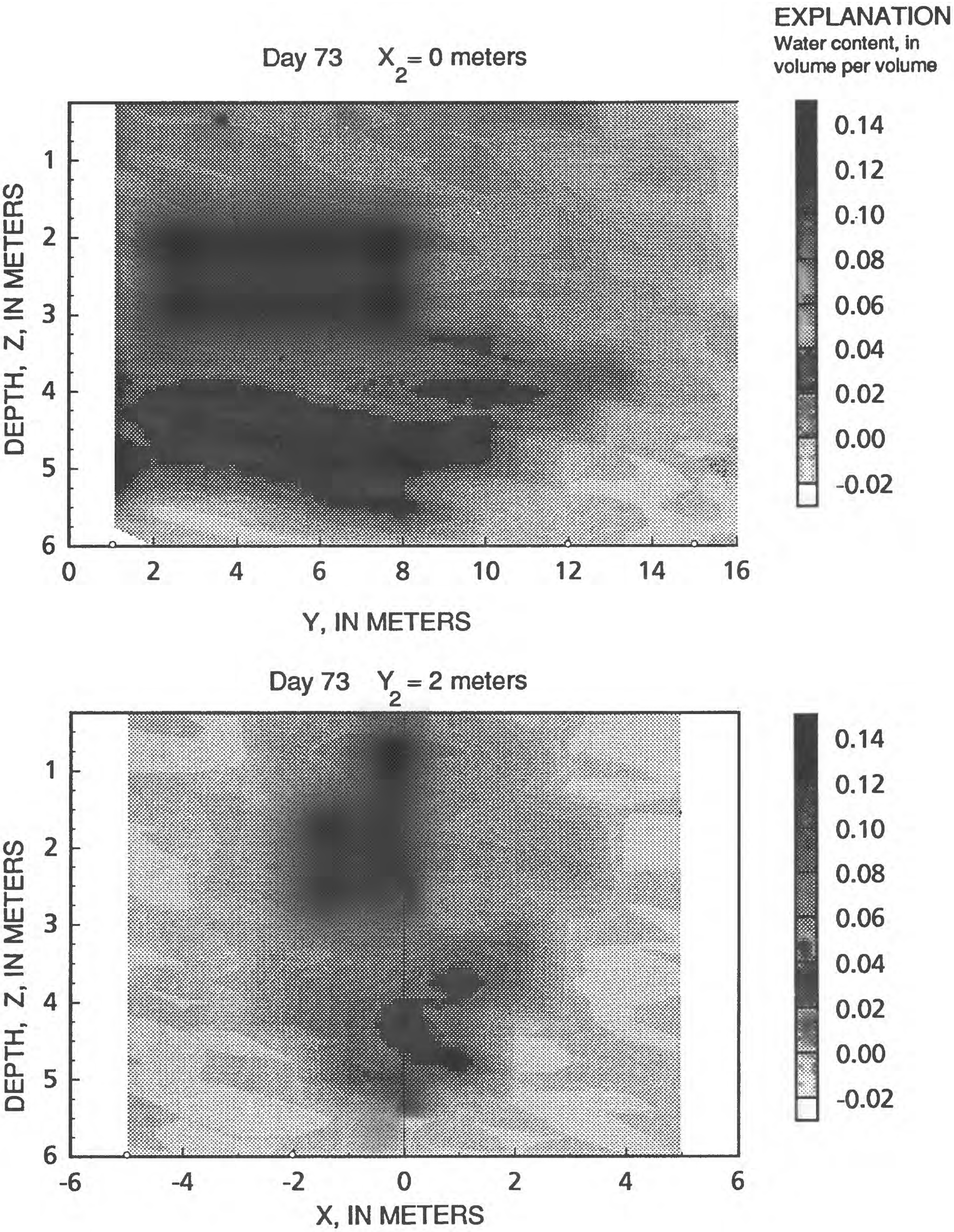

Figure 38. Increases in water contents measured 73 days after start of irrigation on plot 2, for experiment 2b. Top half; water content differences perpendicular to trench wall. Bottom half; water content differences at 2 meters distance and parallel to trench face.

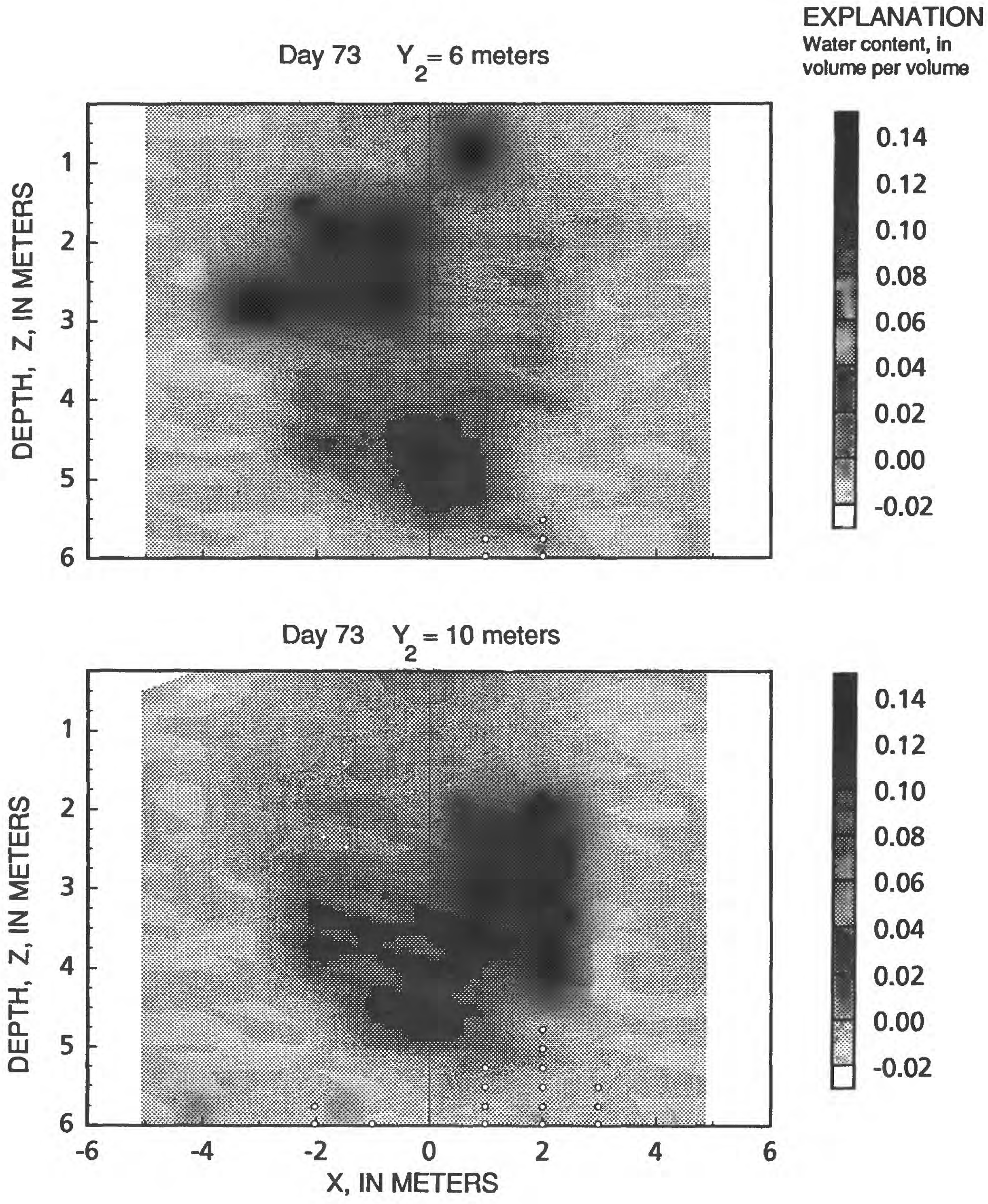

Figure 39. Increases in water contents measured 73 days after start of irrigation on plot 2, for experiment 2b, at 6 meters (top half) and 10 meters (bottom half) from trench face. The squares indicate missing values.

here) obtained from soil coring are also relatively consistent in shape. This indicates that preferential flow in this soil, under these experimental conditions, was not that important. The probable reason for the lack of preferential flow is that the relatively low degree of saturation during water application (<50 percent) and the high tensions (>50 mbar) appear to favor more uniform flow patterns through the soil.

A more complete report on water and tracer movement during experiment 2b is being prepared. The data from experiments 1 and 2a are available and can be transferred from a computer database in Las Cruces using Internet.

Summary

Experiments at the Las Cruces trench site have provided an extensive data set, which may be used to test computer models for predicting water flow and solute transport through unsaturated soil. The data set is relatively complete with respect to initial conditions, boundary conditions, soil hydraulic properties, water content data and solute concentration measurements. The extensive cooperation between experimentalists and modelers in the design and execution of these experiments has led to a much improved model testing effort.

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ANALYSIS OF UNSATURATED FLOW AND TRANSPORT MODELS

By R.G. Hills *and* P.J. Wierenga

Introduction

Three field experiments have been performed by scientists from the University of Arizona and New Mexico State University at the Las Cruces Trench Site to provide data to test deterministic and stochastic models for water flow and solute transport. These experiments were performed in collaboration with INTRAVAL, which is an international effort toward the validation of geosphere models for the transport of radionuclides. INTRAVAL was initiated by the Swedish Nuclear Power Inspectorate. During Phase I of INTRAVAL, qualitative comparisons between experimental data from the first two experiments (the plot 1 and 2a experiments) and model predictions were made through side by side comparisons of contour plots of water contents and solute concentrations. The third Las Cruces Trench experiment (the plot 2b experiment) was designed by scientists from the University of Arizona and New Mexico State University to provide data for more rigorous model testing. Modelers from the various organizations provided predictions of water flow and solute transport to New Mexico State University for analysis. This paper presents a brief overview of the model testing procedures and preliminary results for the plot 2b experiment.

The Plot 2b Experiment

The plot 2b experiment used the same irrigation system and an expanded version of the monitoring systems that were used during the plot 2a experiment (Wierenga and others, these proceedings). Different water application rates and different initial conditions were used. The irrigated area was 1.22 m by 12 m with an average water application rate of 1.82 cm/d during the 70 day irrigation period. Chromium, boron, and PFBA were applied during the first 15 days of irrigation with tritium, bromide, and DFBA applied during days 29 through 44. Detailed descriptions of the experimental procedures used for site characterization and the previous experiments are provided in Wierenga and others (1989, 1990). An overview of the plot 2b experiment and the associated model testing plan is provided in Hills and Wierenga (1991).

The Models

Water content predictions for the plot 2b experiment were provided by the Center for Nuclear Waste Regulatory Analysis, Massachusetts Institute of Technology (MIT), New Mexico State University, Pacific Northwest Laboratory, and the Bureau of Economic Geology at the University of Texas at Austin. Solute transport predictions were provided by New Mexico State University and Pacific Northwest Laboratory. All models for water flow were either based on, or reduced to Richards' equation when applied to the plot 2b experiment. With the exception of the MIT model, the van Genuchten (1980) or modified van Genuchten models were used for the water retention and unsaturated hydraulic conductivity curves. The convection/dispersion equation was used to model solute transport. A summary of the corresponding soil models is provided in table 12.

The predicted data were compared to the experimental data using both point quantities and integrated quantities. The following point quantities were compared:

1. Contour plots of observations versus predictions for water contents and solute concentrations.
2. Scatter plots of observations versus predictions for water contents and solute concentrations.
3. First arrival times of the water and solute plumes as a function of depth.

The following integrated quantities were compared:

1. First and second moments of the water and tritium plumes were evaluated as a function of time.
2. The normalized change in total water volume below each of the z = 0, 1,..., 5 m horizontal planes were evaluated as a function of time. The observed changes in water volume below a horizontal plane is a good estimate of the water that passed through that plane while the plume remains fully observable. The changes in the sum of relative tritium concentrations

Table 12. Modeling of the plot 2b experiment

[BEG, Bureau of Economic Geology, the University of Texas at Austin; CNWRA, Center for Nuclear Waste Regulatory Analysis, Southwest Research Institute; MIT, Massachusetts Institute of Technology; NMSU, New Mexico State University; PNL, Pacific Northwest Laboratory]

Group	Model	Comments
BEG	BEG1	Modeled 2-D, uniform, isotropic soil
CNWRA	CNWRA1	Modeled heterogeneous, isotropic soil in 2-D using trench face characterization
MIT	MIT1	Modeled soil using 3-D effective media stochastic property models in a 2-D simulation
NMSU	NMSU1	Modeled soil as homogeneous, isotropic in 2-D
	NMSU2-NMSU5	Sampled 4 heterogeneous realizations from the observed property field along trench face and modeled in 2-D
PNL	PNL1	Modeled soil as homogeneous, anisotropic in 2-D using modified van Genuchten curves
	PNL2	Modeled soil as homogeneous, anisotropic in 2-D using modified van Genuchten parameters
	PNL3	Modeled soil as homogeneous, isotropic in 2-D using plot 1 infiltration data for calibration
	PNL4	Modeled soil as heterogeneous, isotropic in 2-D using kriged water retention parameters and spatially correlated, random realization of the saturated conductivity, conditioned on the observed property field along the trench face

below each of the $z = 0, 1, \ldots, 5$ m horizontal planes were also evaluated as a function of time.

Here we present only a subset of the water flow results. The complete presentation of results are available in NUREG/CR-5607 and NUREG/CR-5716.

Results

Contour plots of the day 70 water contents for the experiment and several of the models are presented in figures 40 and 41. Note that the heterogeneous models (PNL4, NMSU5) show the effects of spatial variability but do not show as much layering as the experiment does.

Scatter plots of the experimental observation versus model predictions for day 70 are shown in figure 42 for the heterogeneous soil model PNL4 and the uniform soil model NMSU1. If a model predicts the experimental data perfectly, all of the data should lie on a 45 degree line. Clearly, the effects of spatial variability are very pronounced. The lower bound for the initial water content is given by the residual water content ($\theta_r = 0.0828$) for the uniform soil model (NMSU1), and the water content behind the wetting front tends to be somewhat uniform for this model.

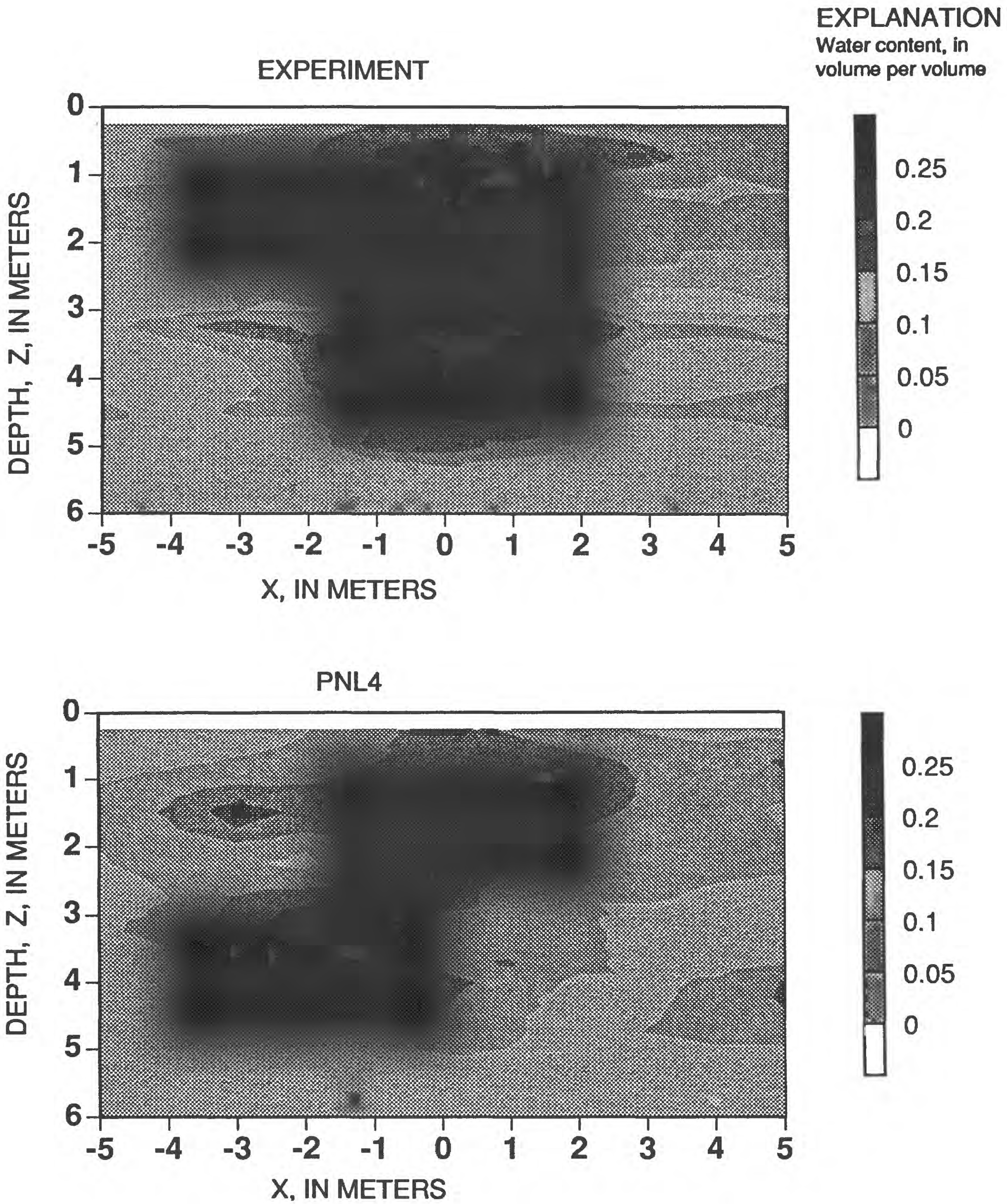

Figure 40. Volumetric water contents on day 70: Experiment and PNL4 model.

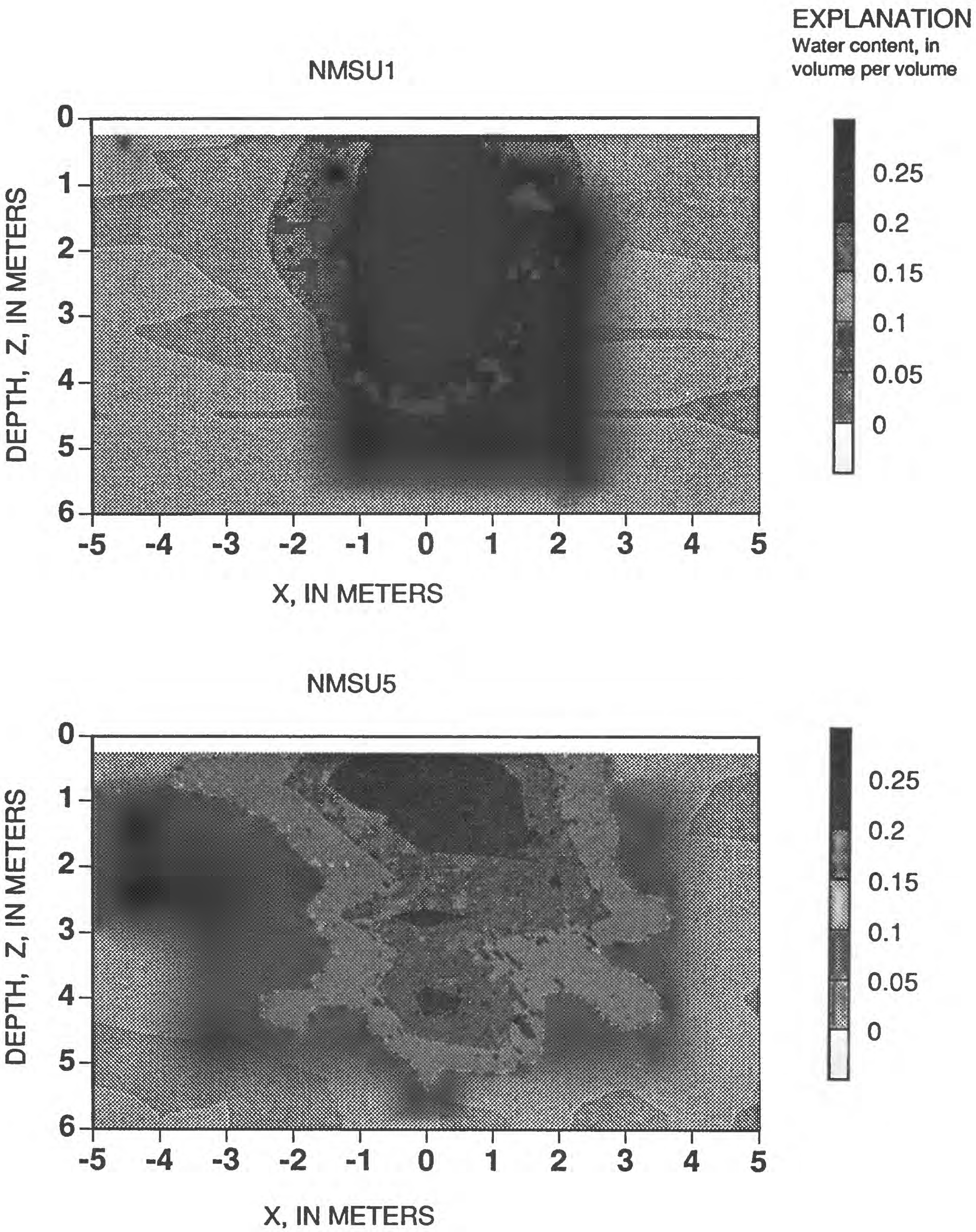

Figure 41. Volumetric water contents on day 70: NMSU1 and NMSU5 models.

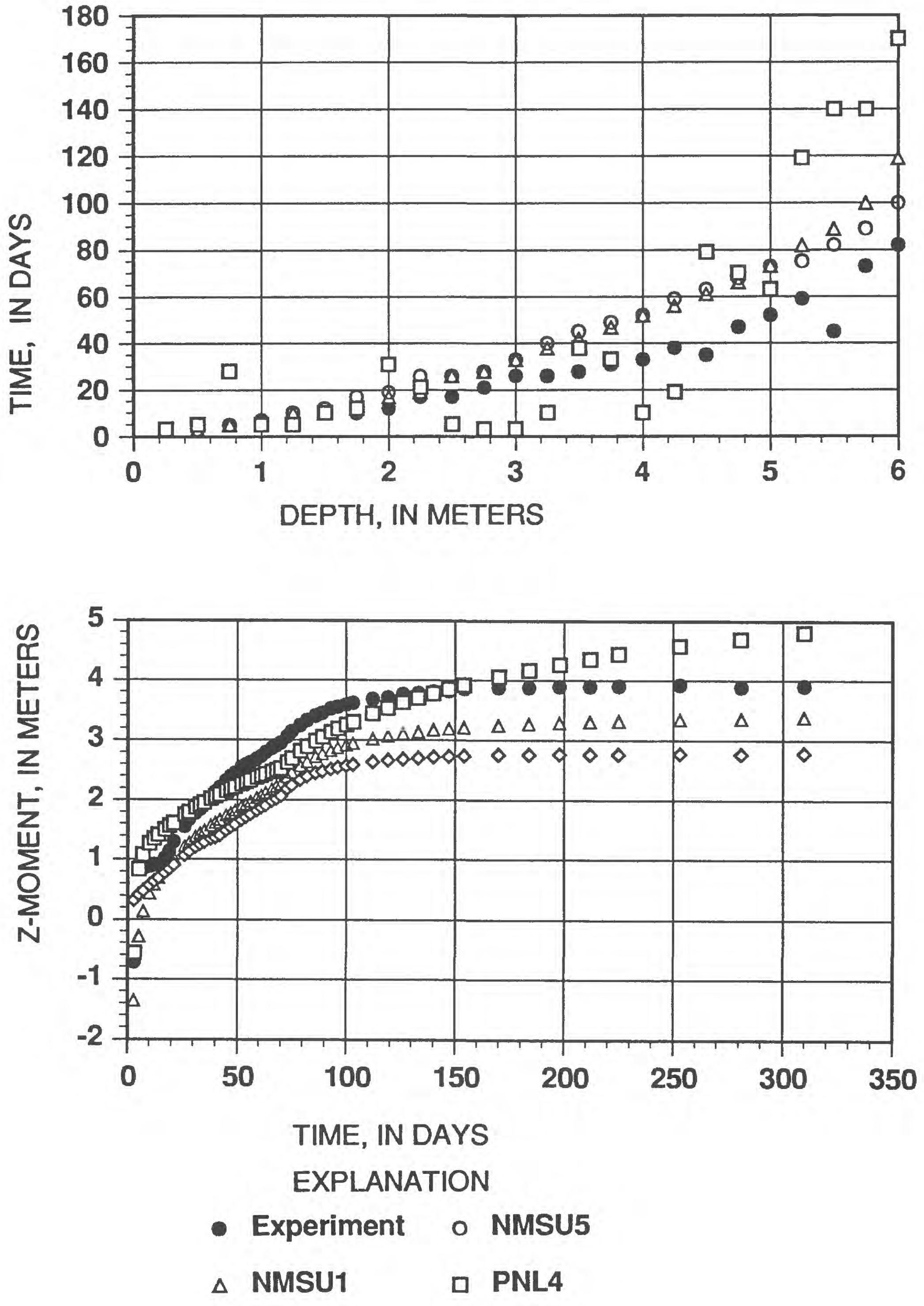

Figure 42. Volumetric water contents on day 70: PNL4 and NMSU1 models.

As a result, there is a clustering of data around the initial conditions and around the wetter conditions behind the front. In contrast, the PNL4 heterogeneous model shows less clustering.

Time of first arrival of the water plume (defined as the time when the local volumetric water content increases by 0.03) as a function of depth is shown in figure 43 for several of the models. Note that even though there is considerable scatter in the scatter plots of figure 41, the first arrival times of figure 43 show clear trends. All of the models under predicted first arrival times below 4.5 m. Thus, none of the models are conservative. The most conservative model shown is NMSU5. However, this is just one of four realizations of the NMSU2-NMSU5 models and this realization is based on the property field that was taken furthest (approximately 14 m) from the irrigation centerline. The *z* moments of the water plumes are also shown in figure 43. PNL4 over predicts the plume movement at latter times while the two NMSU models under predict this movement.

Conclusions

As the results presented here indicate, there are considerable differences in model predictions. Some of the models presented were fairly simple and assumed uniform soils while others conditioned the soil models on spatial heterogeneities observed in the trench face. Based on the results presented, several preliminary observations can be made.

1. Even though many models were considered, none of the models stood out as clearly superior.
2. Models that perform well by one measure may not perform as well by another.
3. Times of first arrivals of the water plume were greater for the experiment than for any of the models once the plume reached 4.5 m. This indicates that none of the models provided a conservative estimate of arrival time. While this was expected for the uniform soil models, it was not expected for the heterogeneous models.

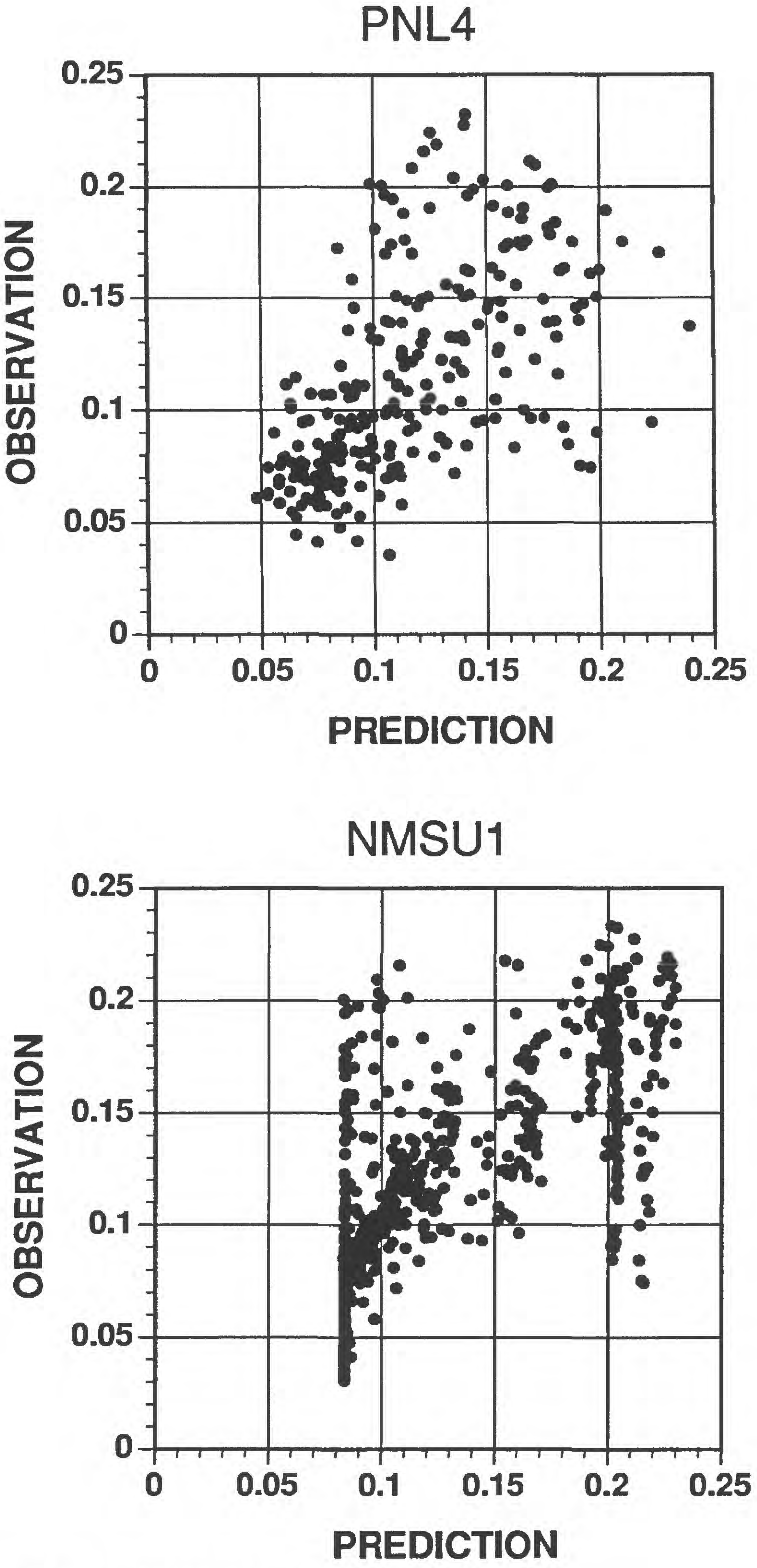

Figure 43. Time of first arrivals (top) and z-moments (bottom).

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STOCHASTIC FLOW AND TRANSPORT MODELING IN THE UNSATURATED ZONE

By Lynn W. Gelhar

This topic is addressed in a recent book and U.S. Nuclear Regulatory Commission report. Interested individuals should refer to:

Gelhar, L.W., 1993, Stochastic subsurface hydrology: Englewood Cliffs, New Jersey, Prentice-Hall, Inc., 385 p.

Gelhar, L.W., Celia, M.A., and McLaughlin, D., 1994, Modeling field scale unsatured flow and transport processes: Washington, D.C., U.S. Nuclear Regulatory Commission, NUREG/CR-5965, 66 p.

CONSIDERATIONS OF SCALE AND INFORMATION CONTENT IN SUBSURFACE FLOW AND TRANSPORT MODELING

By S.P. Neuman *and* D. Zhang

Introduction

Flow and transport parameters such as hydraulic conductivity, seepage velocity, and dispersivity have been traditionally viewed as well-defined local quantities that can be assigned unique values at each point in space (and possibly time). Yet in practice these parameters can at best be measured at selected well locations and depth intervals, where their values depend on the scale (support volume) and mode (instruments and procedure) of measurement. Estimating the parameters at points where measurements are not available entails a random error. Quite often, the support of the measurements is uncertain and the data are corrupted by experimental and interpretive errors. These errors and uncertainties render the parameters random and the corresponding flow and transport equations stochastic. The stochastic flow and transport equations can be solved numerically by (conditional) Monte Carlo simulation but this may be very demanding computationally. Are deterministic flow and transport models a viable alternative? We present deterministic equations which do offer such an alternative by providing optimum predictions of flow and transport in light of the available data and associated uncertainty. These equations differ from traditional deterministic flow and transport equations (which are therefore not optimal) both in form and in the nature of their parameters. The optimal equations involve integrals and spatially varying local and nonlocal parameters (the latter depending on more than one point in space and /or time). The traditional concept of an REV (representative elementary volume) is neither necessary nor relevant for their validity or application. The parameters are nonunique in that they depend not only on local medium properties but also on the information one has about these properties (scale, location, quantity, and quality of data). Darcy's law and Fick's analogy are generally not obeyed by the flow and transport predictors except in special cases or as approximations. Such approximations yield familiar-looking differential equations in which however the hydraulic conductivity, seepage velocity, and dispersivity are nonunique, information-dependent parameters. We demonstrate this dependence by numerical examples of two-dimensional transport. Our examples show that the stochastically derived deterministic theory provides not only predictions of flow and transport, but also measures of the associated prediction uncertainty.

Stochastically-Derived Deterministic Equations of Flow

Continuum subsurface flow models are usually based on the premise that Darcy's law applies at each point x in a geologic medium. This implies the existence of a hydraulic conductivity as a unique function of space, K(x). Spatial variations in hydraulic conductivity (and porosity) produce spatial fluctuations in head, velocity, and solute concentration which cannot be predicted with certainty without knowing K(x) at each x. In practice, K(x) can at best be measured at selected well locations and depth intervals where its values depend on the scale (support volume) and mode (instruments and procedure) of measurement. Quite often, the support of the measurements is uncertain and the data are corrupted by experimental and interpretive errors. Estimating K(x) at points where measurements are not available entails an additional random error. These errors and uncertainties render K(x) random and generally unknown. For simplicity, we assume below that all measurement of K(x) represent rock samples of equal volume (support), ω. Let k(x) be a relatively smooth and unbiased estimate of K(x) obtained from these data by a method such as, say, kriging. Then the unknown K(x) differs from the known (deterministic) k(x) by a random error K′(x),

$$K'(x) \equiv K(x) - k(x) \; . \tag{7}$$

Though this error is unknown, its mean is by definition zero and its spatial covariance can often be inferred from the data (Neuman and Orr, 1993).

We write Darcy's law as

$$q(x) = -K(x)\nabla h(x) \tag{8}$$

where q(x) is a flux vector and ∇h(x) a hydraulic head gradient across a rock volume ω centered about x. We take h(x) to satisfy the steady-state flow equation

$$\nabla \cdot [K(x)\nabla h(x)] + f(x) = 0 \tag{9}$$

subject to the boundary conditions

$$h(x) = H(x) \tag{10}$$

$$-q(x) \cdot n(x) = Q(x) \tag{11}$$

where f(x) is a randomly prescribed source function, H(x) is a randomly prescribed head function, Q(x) is a randomly prescribed flux function, and n(x) is a unit vector normal to the boundary, pointing outward. It is most important to note that ω need not constitute a representative elementary volume (an REV) for equations (8) - (11) to hold; in fact, an REV need not even exist. The only requirement is that all the quantities which enter into these equations be defined and/or measured on the same support, ω (Baveye and Sposito, 1985; Neuman, 1987). As K(x) is scale-dependent and random, so will be the heads and fluxes computed with these equations. In other words, equations (8) - (11) constitute a system of stochastic equations.

The most straight-forward way to solve stochastic differential equations is numerically by (conditional) Monte Carlo simulation. A major disadvantage of this approach is that it requires much computer time and storage. Another disadvantage is that numerical methods provide little if any theoretical insight into the nature of the solution. We therefore ask: Is a deterministic flow model a viable alternative? If so, what kind of a deterministic model would be appropriate? An answer to these questions has been given by Neuman and Orr (1993). These authors recognized that the best deterministic predictors of the unknown random functions h(x) and q(x) are their conditional ensemble means $\langle h(x)\rangle_k$ and $\langle q(x)\rangle_k$, respectively. Here $\langle\,\rangle$ designates ensemble mean and the subscript *k* indicates that the mean is conditioned on the same K(x) data as those used to obtain the estimate *k*(x). In other words, the conditional mean $\langle\,\rangle_k$ honors all measured values of K(x) to within their measurement (and/or interpretive) error. This is not so for the unconditional mean $\langle\,\rangle$ which is the moment of interest in much of the current stochastic ground-water literature. Neuman and Orr have shown that $\langle h(x)\rangle_k$ and $\langle q(x)\rangle_k$ satisfy exactly the deterministic flow equation

$$\nabla \cdot \left[k(x)\nabla\langle h(x)\rangle_k - r_k(x)\right] + \langle f(x)\rangle = 0 \tag{12}$$

subject to the deterministic boundary conditions

$$\langle h(x)\rangle_k = \langle H(x)\rangle \tag{13}$$

$$-\langle q(x)\rangle_k \cdot n(x) = \langle Q(x)\rangle \tag{14}$$

where $\langle f(x)\rangle$, $\langle H(x)\rangle$, and $\langle Q(x)\rangle$ are prescribed (unconditional) first moments of the statistically independent random source and boundary terms, and $r_k(x)$ is a residual flux vector. The latter is given by integrals containing head gradients at points other than x and is therefore generally non-Darcian and nonlocal. It is clear from equation (12) that *k*(x), the best available estimate of the unknown function K(x), does not act as an effective hydraulic conductivity in the deterministic problem formulation. In fact, since $r_k(x)$ is generally non-Darcian, such an effective conductivity does not strictly exist except in special cases of limited interest. Hence the traditional reliance by ground-water hydrologists on deterministic flow models with effective hydraulic conductivities is not strictly justified in most cases. This explains why, though one may be able to fit effective parameters to data representing a specific flow regime by model calibration, one often finds that the fit deteriorates when additional data become available which represent different flow regimes in the same aquifer (Carrera and others, 1990).

The integrals that make up $r_k(x)$ contain kernels which act as nonlocal system parameters. These parameters as well as $k(x)$ are functions not of K(x) but of what is known and unknown about K(x). In other words, the parameters are functions of the scale, location, quantity, and quality of the available hydraulic-conductivity measurements and the statistics of the K(x) field as inferred from these data. As such, the parameters entering into the deterministic flow equation (12) are nonunique. They do not represent strictly material properties, but depend additionally on information. This helps explain why the results of deterministic model calibration tend to vary continuously as more and more data are incorporated in the model.

As the information content of the data (their quantity and quality) increases, the magnitude of $r_k(x)$ diminishes. The same happens to the estimation error associated with $k(x)$ and to the prediction errors associated with $\langle h(x)\rangle_k$ and $\langle q(x)\rangle_k$. In the hypothetical limit where perfect and complete data concerning K(x) become available, $r_k(x)$ vanishes, $k(x)$ becomes perfect representation of K(x), and $\langle h(x)\rangle_k$ and $\langle q(x)\rangle_k$ approach h(x) and q(x) to within an error that depends on how well the deterministic forcing terms $\langle f(x)\rangle$, $\langle H(x)\rangle$, and $\langle Q(x)\rangle$ represent their true counterparts f(x), H(x), and Q(x), respectively.

As information content increases, the distances over which nonlocality acts diminish. The shorter are these distances, the more appropriate it may be to approximate the mean hydraulic gradients across them by constants. This in turn allows approximating $r_k(x)$ by

$$r_k(x) \cong \tilde{k}(x)\,\nabla\langle h(x)\rangle_k \qquad (15)$$

where $\tilde{k}(x)$ is a local symmetric, positive semi-definite tensor. One then obtains the Darcian form

$$\langle q(x)\rangle_k \cong -K_{ek}(x)\,\nabla\langle h(x)\rangle_k \qquad (16)$$

where

$$K_{ek}(x) = k(x)\mathrm{I} - \tilde{k}(x) \qquad (17)$$

is a conditional effective hydraulic conductivity tensor, I being the identity tensor. Note that our definition of effective hydraulic conductivity differs from those found in the literature. Our $K_{ek}(x)$ is a function of space and can have different principal values and directions at different points. It is not an upscaled tensor but a local tensor defined on the scale of ω, relating the predicted flux to the predicted head gradient on this same scale. It is a function of medium properties and information (hence the adjective "conditional").

Equations (12) - (14) constitute an exact deterministic system of equations which can be solved for the predictors $\langle h(x)\rangle_k$ and $\langle q(x)\rangle_k$, subject to arbitrary random source and boundary terms, provided either that the kernels of $r_k(x)$, or $\tilde{k}(x)$ when equation (15) is applicable, are known. Since these (nonlocal or local) parameters as well as the local parameter $k(x)$ and the functions $\langle h(x)\rangle_k$ and $\langle q(x)\rangle_k$ are smooth relative to their random counterparts, they can be treated approximately as finite dimensional functions, that is, each can be expressed as the linear combination of a finite number of basis functions in the standard manner of finite elements; such methods can then be used to solve equations (12) - (14). The dimensionality N of each approximating function, that is, the number N of basis functions employed (which controls the number of nodes and elements in a finite element grid), should depend in a standard way on the degree of smoothness of the function being approximated. Though we defer detailed discussion of this topic to future papers, we nevertheless see that the theory provides a direct answer to the important question how should the scale of grid discretization (N) relate to the scale of measurement (ω) and to the quantity and quality of available data (smoothness of conditional moments).

Stochastically-Derived Deterministic Equations of Transport

The advective (seepage) velocity of ground water that controls solute transport is related to the Darcy flux through $v = q/ø$ where ø is kinematic (effective) porosity. Since the hydraulic conductivity and porosity are uncertain (random), so is the seepage velocity. The latter is difficult to measure directly and so its statistical properties must usually be inferred by solving the stochastic flow equations (9) - (11), or their transient equivalents, based on measurements of K and ø on supports of order ω. The task is somewhat simplified by the fact that ø tends to fluctuate more slowly in space than does K and is therefore often treated as a known function. In what follows, we consider v(x,t) to be a function of both space and time and postulate that analogy to Fick's first law applies so that

$$J(x,t) = v(x,t)c(x,t) - D_l \nabla c(x,t) \tag{18}$$

when the solute mass flux J(x,t), the local dispersion tensor D_l, the concentration c(x,t) and its gradient ∇c(x,t) are representative of ω. Mass conservation yields Fick's second law

$$\frac{\partial c(x,t)}{\partial t} + \nabla \cdot J(x,t) = g(x,t) \tag{19}$$

where g(x,t) is a solute source term on the scale of ω. To keep matters relatively simple, we restrict consideration to an unbounded flow domain with zero initial concentration, consider g(x,t) to be random with independently prescribed statistical properties, and set D_l equal to zero. However, rather than requiring that $\nabla \cdot v = 0$ as is common in the stochastic ground water literature, we allow the fluid velocity to satisfy a transient flow equation

$$\nabla \cdot v(x,t) = p(x,t) \tag{20}$$

where p(x,t) is a random fluid source function and/or an accumulation term involving $\partial h/\partial t$. Equations (18) - (20) are stochastic.

Let υ(x,t) be relatively smooth and unbiased estimate of the unknown random function v(x,t) obtained by solving the stochastic flow equation (20). Methods to compute the deterministic function υ(x,t) include averaging the results of conditional Monte Carlo flow simulations, or the solution of conditional moment equations such as those we have presented earlier for steady state. The unknown true (on the scale of ω) seepage velocity v(x,t) differs from the known estimate υ(x,t) by a random error v'(x,t),

$$v'(x,t) = v(x,t) - \upsilon(x,t)\,. \tag{21}$$

Through this error is unknown, its mean is by definition zero and its higher (at least second) moments are obtained in the process of solving equation (20). It has been pointed out by Neuman (1993a) that the best deterministic predictors of the unknown random functions c(x,t) and J(x,t) are their conditional ensemble means $\langle c(x,t)\rangle_\upsilon$ and $\langle J(x,t)\rangle_\upsilon$, respectively. Here the subscript υ indicates conditioning on those data used to obtain $\upsilon(x,t)$. The author has shown that $\langle c(x,t)\rangle_\upsilon$ and $\langle J(x,t)\rangle_\upsilon$ satisfy exactly the deterministic transport equation

$$\frac{\partial\langle c(x,t)\rangle_\upsilon}{\partial t} + \nabla\cdot\langle J(x,t)\rangle_\upsilon = \langle g(x,t)\rangle \qquad (22)$$

subject to the initial condition $\langle c(x,0)\rangle_v \equiv 0$ where

$$\langle J(x,t)\rangle_\upsilon = \upsilon(x,t)\langle c(x,t)\rangle_\upsilon + Q_\upsilon(x,t) \qquad (23)$$

and $Q_\upsilon(x,t)$ is a (deterministic) dispersive solute mass flux. The latter is given by space-time integrals containing the concentration and its gradients at points other than x and at times other than t. As such, $Q_\upsilon(x,t)$ is generally non-Fickian and nonlocal. Hence the traditional reliance by ground-water hydrologists on deterministic transport models with Fickian dispersion coefficients is not strictly justified in most cases (as is well known from the observed increase in real and apparent dispersivity with mean travel distance (Freyberg, 1986; Dagan, 1987; Neuman, 1990, 1991, 1993b)). Likewise, hydrologists are not justified viewing the advective velocity $\upsilon(x,t)$ in deterministic transport equations as actual seepage velocity v(x,t): the former is only a smooth estimate of the latter.

The integrals that make up $Q_\upsilon(x,t)$ contain kernels which act as space-time nonlocal system parameters. These parameters as well as the advective velocity $\upsilon(x,t)$ are functions not of actual flow conditions but of what is known and unknown about these conditions. In other words, the transport parameters depend on the scale, location, quantity, and quality of available data and on statistics inferred from these data. As such, the parameters are nonunique. They do not represent strictly material properties but are additionally functions of information. As the information content of the data (their quantity and quality) increases, $\upsilon(x,t)$ becomes a better estimate of the unknown true velocity v(x,t), and the magnitude of the dispersive flux $Q_\upsilon(x,t)$ diminishes. The same happens to the prediction errors associated with $\langle c(x,t)\rangle_\upsilon$ and $\langle J(x,t)\rangle_\upsilon$. In the hypothetical limit where perfect and complete data concerning v(x,t) become available, $Q_\upsilon(x,t)$ vanishes (assuming absence of local dispersion), and $\langle c(x,t)\rangle_\upsilon$ and $\langle J(x,t)\rangle_\upsilon$ approach c(x,t) and J(x,t) to within an error that depends on how well the unconditional deterministic source term $\langle g(x,t)\rangle$ represents its true counterpart g(x,t). This helps explain why dispersivities obtained from the calibration of deterministic Fickian transport models diminish as more detail about spatial permeability variations (information about heterogeneity, which allow a more refined description of velocity variations) is built into the model (Neuman, 1990, 1991, 1993b; Jensen and others, 1993).

Consider the special case where the fluid source p(x,t) in equation (20) is known with certainty. If one introduces a slug of solute into the medium at point x_0 instantaneously at time t_0, and if the velocity estimation errors $v'(x,t)$ are autocorrelated over finite space-time intervals (as is often the case after conditioning), one can define a conditional Lagrangian correlation time $\tau_\upsilon(x_0,t_0)$ which measures the time after which a hypothetical particle representing the slug loses all memory of its velocity at t_0 (more precisely, the particle velocity at time $t > t_0 + \tau_\upsilon$ is essentially uncorrelated with that at time t_0). For solute residence times $t - t_0$ in excess of $\tau_\upsilon(x_0,t_0)$, the dispersive flux can be approximated by (Neuman, 1993a)

$$Q_\upsilon(x, t;x_0, t_0) \cong -D_\upsilon(x, t;t_0)\,\nabla\langle c\,(x, t|x_0, t_0)\rangle_\upsilon \tag{24}$$

where $D_\upsilon(x,t;t_0)$ is a space-time dependent conditional dispersion tensor and $c(x,t|x_0,t_0)$ is concentration due to the instantaneous point source. The approximation is termed pseudo-Fickian to indicate that, contrary to the Fickian case, the dispersion tensor is nonlocal in time (varies with residence time, in addition to being a function of spatial location). When the conditional Lagrangian correlation time $\tau_\upsilon(x_0,t_0)$ is finite, $D_\upsilon(x,t;t_0)$ becomes asymptotically independent of t_0 and tends to some local (Fickian) value $D_\upsilon^\infty(x,t)$. This happens either as (t---t_0) continues to grow or as $\tau_\upsilon(x_0,t_0)$ shrinks in comparison to a given $(t - t_0)$ due to an improvement in the quality of the estimate $\upsilon(x,t)$. It is thus clear that under both pseudo-Fickian and Fickian conditions, the dispersion tensor depends both on the velocity field $v(x,t)$ and on information (hence the adjective "conditional") concerning this field.

In the unconditional case where $\upsilon \equiv \langle v\rangle$ = constant and $v'(x,t)$ is second-order stationary in space-time (has a location-independent covariance), the dispersion coefficient becomes strictly a function of residence time, $D(t - t_0)$, as in the theories of Taylor (1921), Dagan (1987), Neuman and Zhang (1990), and Zhang and Neuman (1990). The concentration and pseudo-Fickian dispersive flux become strictly functions of distance from the source and residence time

$$Q(x-x_0,t-t_0) \cong -D(t-t_0)\ \nabla\langle c\,(x-x_0, t-t_0)\rangle\ . \tag{25}$$

As $(t - t_0)$ increases while the Lagrangian correlation time remains finite, $D(t - t_0)$ tends asymptotically to a Fickian constant, D^∞.

In the case of a known initial concentration $c(x,0)$ with a slowly varying gradient where no sinks or sources of solute are active a $t > 0$, the pseudo-Fickian approximation can be invoked starting with time zero,

$$Q_\upsilon(x,t) \cong -D_\upsilon(x,t)\nabla\langle c(x,t)\rangle_\upsilon \tag{26}$$

where $D(x,t) \equiv D(x,t;0)$.

Computational Examples of Two-Dimensional Transport

We have developed a combined analytical-numerical method of solving the deterministic transport equations (22) - (23) which avoids dealing with spatial nonlocality. This is accomplished by extending the application of a known early time analytical solution, and that of the pseudo-Fickian expression (24), into the intermediate time domain where the two solutions are matched. To render our analysis even simpler, we have so far restricted it to mildly heterogenous media in which the unconditional log hydraulic conductivity variance does not exceed one. This enables us to linearize the pseudo-Fickian dispersion coefficient about conditional mean trajectories, to use available analytical expressions for the unconditional Eulerian velocity covariance obtained by linearizing the stochastic flow equation, and to condition this covariance on log hydraulic conductivity and/or head data via cokriging. We solve the linearized pseudo-Fickian transport equation by a Galerkin finite element scheme. As the conditional dispersion coefficient is initially zero (when local dispersion is disregarded), the corresponding Peclet number is initially infinite. Our use of an analytical solution at early time helps us avoid numerical difficulties commonly encountered with large Peclet numbers. The approach also allows us to compute explicitly the conditional variance (and coefficient of variation) of the concentration prediction error and other quantities of interest including (among others) conditional plume spatial moments, conditional travel time distributions, conditional cumulative mass release to the environment across a given compliance surface, and the associated prediction variance. Details of the computational method are being published elsewhere.

To illustrate the method, we start with an unconditional example concerning two-dimensional transport due to an instantaneous source of unit mass under uniform mean steady-state flow. We take the log transmissivity $Y = ln\ T$ to be a statistically homogeneous and isotropic field with zero unconditional mean $\langle Y\rangle$, unit unconditional variance σ_Y^2 , and unit spatial correlation (integral) scale λ. The effective porosity ø is arbitrarily taken to be one. Transport takes place in a domain of size 20λ by 10λ at a uniform mean velocity $\langle v_1 \rangle = 0.1$ parallel to x_1 under a mean hydraulic gradient of 0.1 The dimensionless time interval Δt_υ-=-$\langle v_1\rangle\Delta t/\lambda$ is chosen to be 0.1 The velocity is taken to be normally distributed and pore scale dispersion is neglected.

Figure 44 depicts the predicted evolution of a plume emanating from an instantaneous point source introduced at time $t = 0$ at the origin of the dimensionless space coordinates $X = x_1/\lambda$, $Y = x_2/\lambda$. The upper left plot shows arrows representing the unconditional uniform mean velocity at points corresponding to our finite element grid (not shown). The remaining plots are contours of mean concentration at dimensionless time $t_\upsilon = \langle v_1\rangle t/\lambda = 1, 3, 5, 7$, and 9. For ease of reading, contours are labeled by integer "level" which relates to mean (predicted) concentration as shown in the legend. The contours delineate smooth and regular ellipses corresponding to a Gaussian mean concentration plume, traveling with the mean velocity. These contours correspond exactly to those predicted analytically by the pseudo-Fickian stochastic theory of Dagan (1987), attesting to the accuracy of our computational procedure. Since local dispersion is neglected in this example, the actual plume is strictly a point (or particle) of unit mass and infinite concentration (a dirac delta pulse). The predicted contours greatly exaggerate the spread of this mass, reflecting uncertainty about its actual trajectory: they căn be viewed as the probability of finding the particle at any given point in space-time. The spread (dispersion) predicted by the deterministic transport model clearly does not represent physical mixing (which has been suppressed upon disregarding local dispersion) but rather uncertainty about the actual path taken by the solute.

To further quantify this uncertainty, we show in the upper left plot of figure 45 how the longitudinal (Ω_{11}) and transverse (Ω_{22}) spatial displacement covariances of the particle vary with t_υ. Our numerical values are indistinguishable from those predicted analytically by Dagan (1987). The remaining plots are contours of lower bounds on the concentration coefficient of variation. This lower bound is zero at the plume center and increases consistently with distance from the center. Hence predictive uncertainty is largest at the plume margins where concentrations are lowest.

To see what conditioning does to the predictions, we assume that log transmissivity has been measured at the 5 x 5 locations shown in the upper left part of figure 46. The data are specified as deviations from the mean, or residuals, $Y' = \ln T - \langle \ln T \rangle$. Their most immediate effect is to alter the (originally uniform) mean velocity field as shown in the upper left part of figure 47. The conditional mean streamlines are attracted toward confirmed high transmissivity zones and away from confirmed low transmissivity zones. Hence the predicted plume no longer travels along the unconditional uniform mean trajectory but along a curved conditional

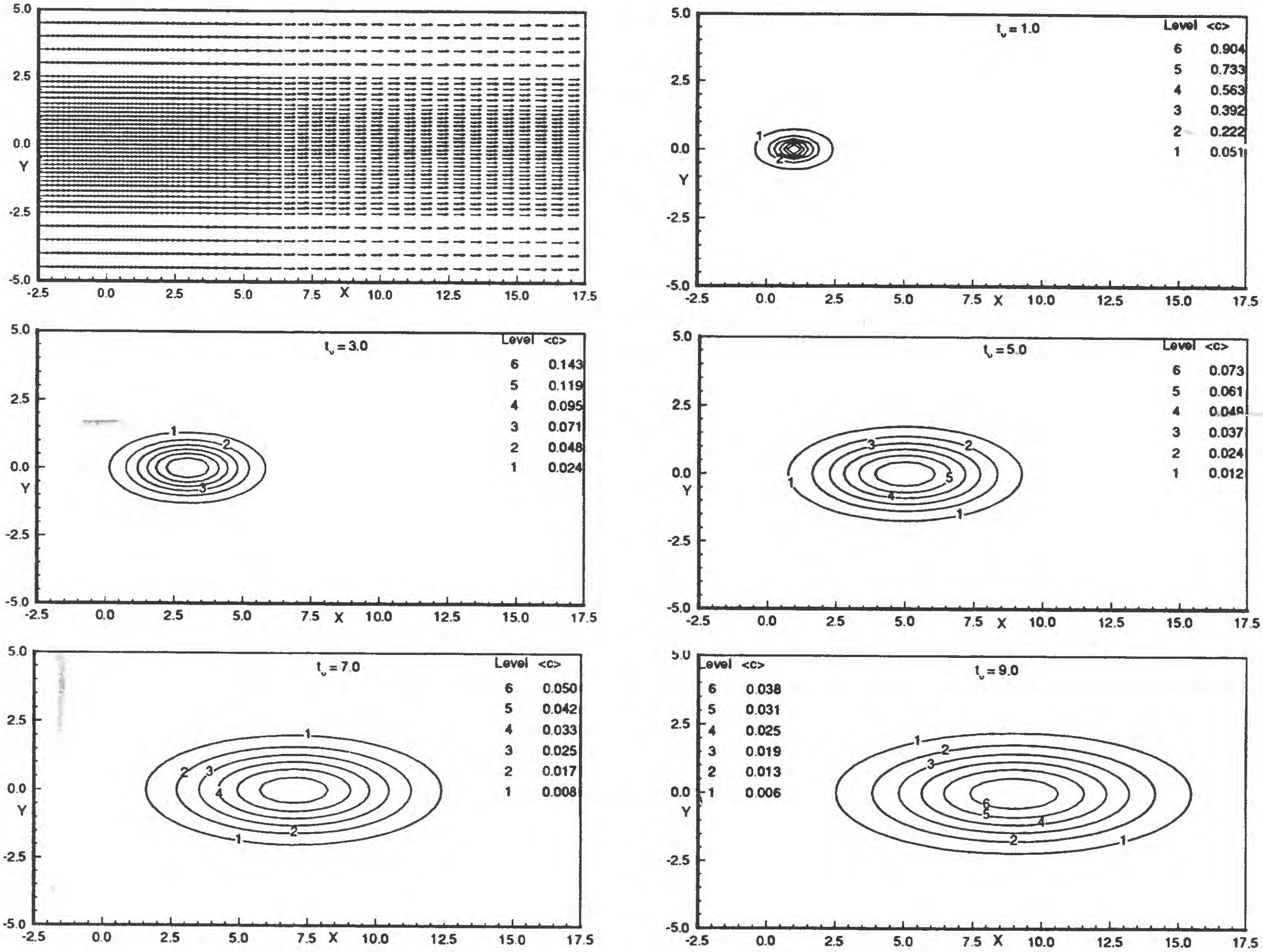

Figure 44. Unconditional mean velocity (upper left) and mean concentration at various dimensionless times due to an instantaneous point source at (0,0). See text.

mean trajectory which represents more closely the (still unknown) true velocity field. The conditional dispersion coefficient differs from its unconditional counterpart in that it depends on location, not only on time. For this reason, the predicted plume contours are no longer standard symmetric ellipses but distorted asymmetric ones. Comparison with figure 44 reveals that areas of high mean concentration inside contour level 6 are now larger than they were in the unconditional case. This illustrates that conditioning reduces the predicted spread, or dispersion, of the plume as anticipated by us on theoretical grounds. Figure 47 shows how the lower bound conditional coefficient of variation varies with dimensionless location and time. Conditioning is seen to cause a greater amount of distortion in these contours than in those of the conditional mean concentration.

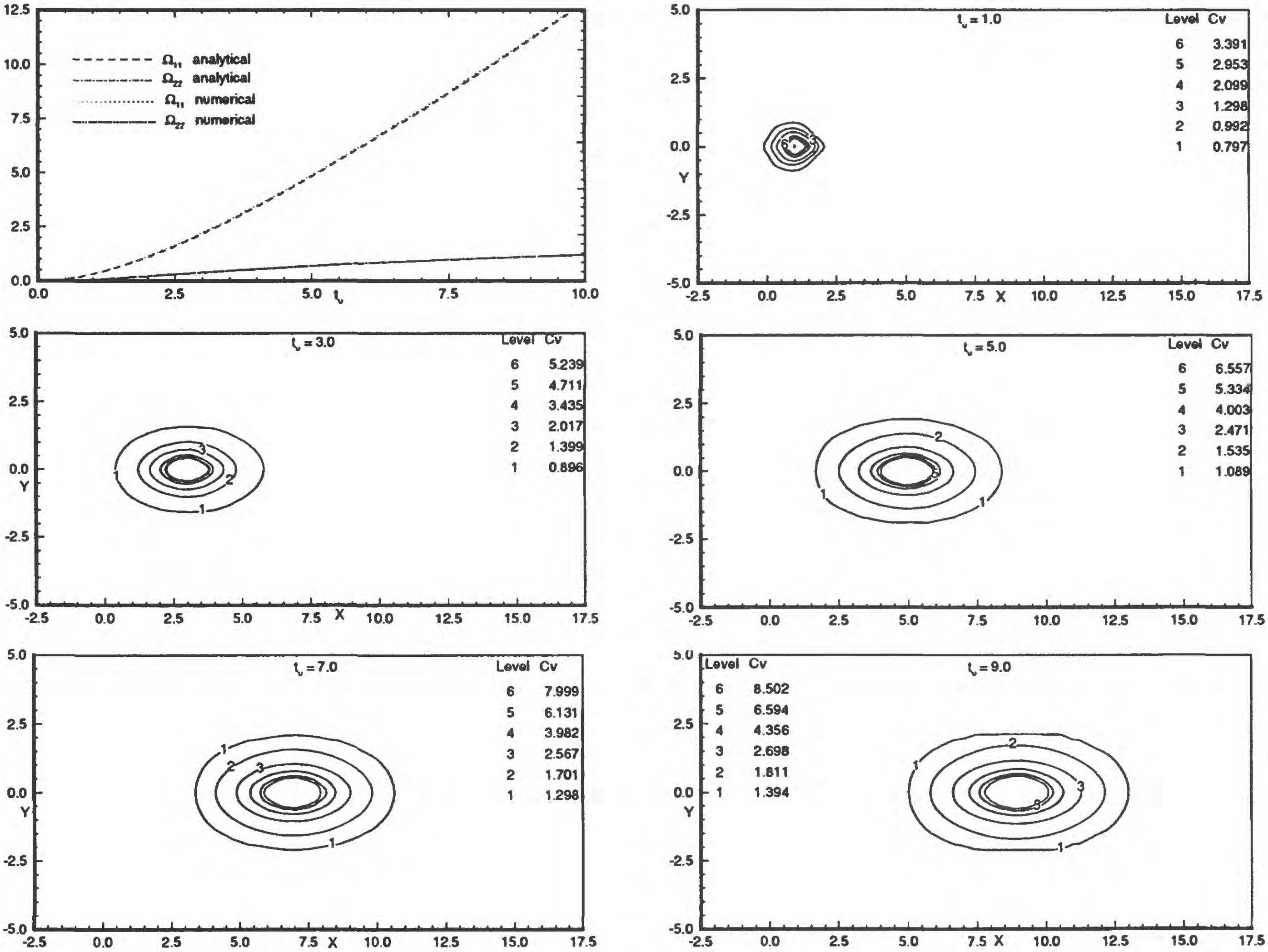

Figure 45. Longitudinal (Ω_{11}) and transverse (Ω_{22}) spatial particle covariance versus dimensionless time (upper left) and lower bound concentration coefficient of variation (Cv) at various dimensionless times due to a point source at (0,0). See text.

Space does not permit us to illustrate here more than just these very elementary aspects of our theory. The power of this theory extends much farther and will be explored in upcoming publications.

Acknowledgments

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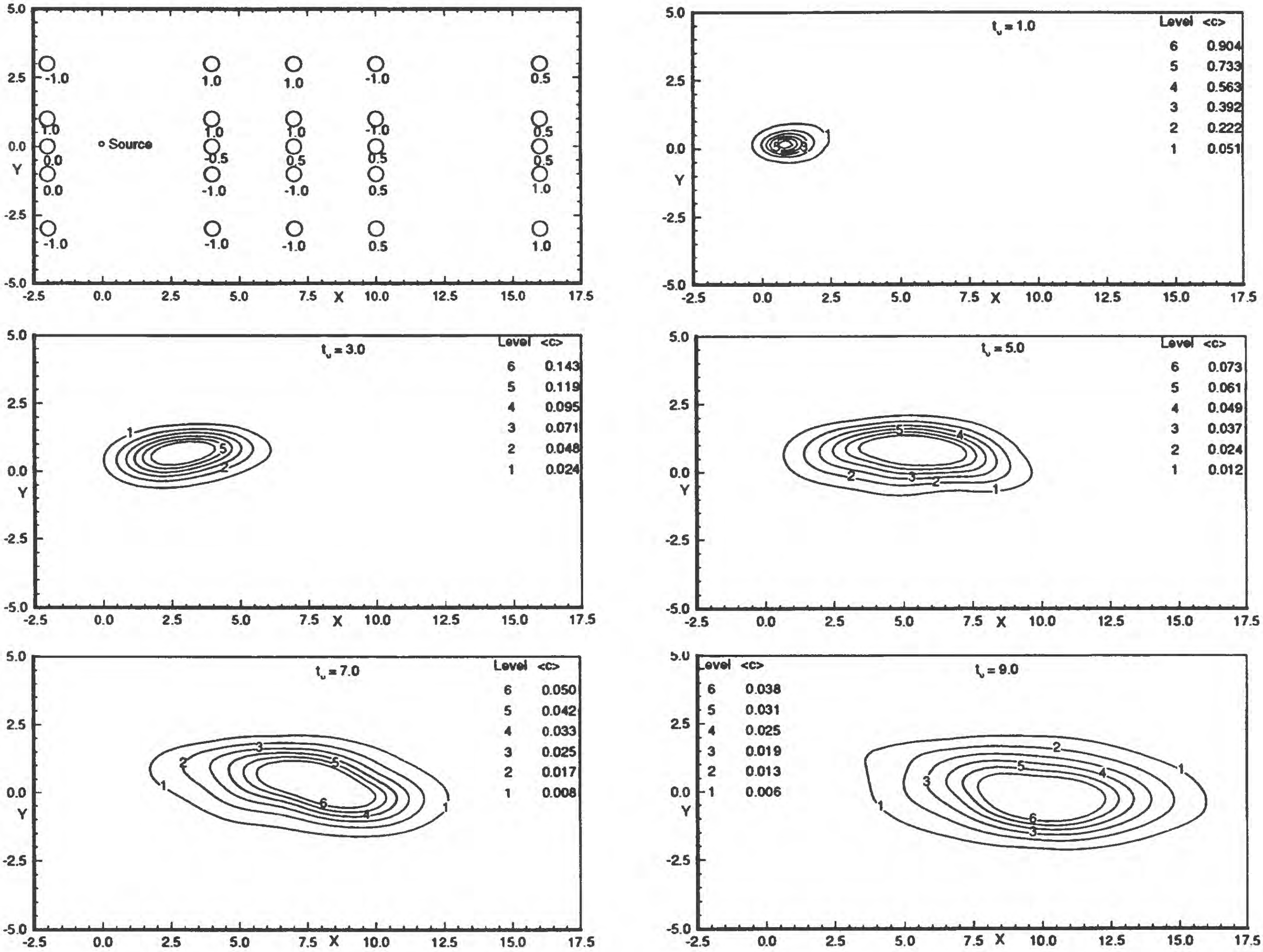

Figure 46. 5 x 5 grid of measured log transmissivity residuals (upper left) and corresponding conditional mean concentration at various dimensionless times due to an instantaneous point source (conditional on 5 x 5 Y' data). See text.

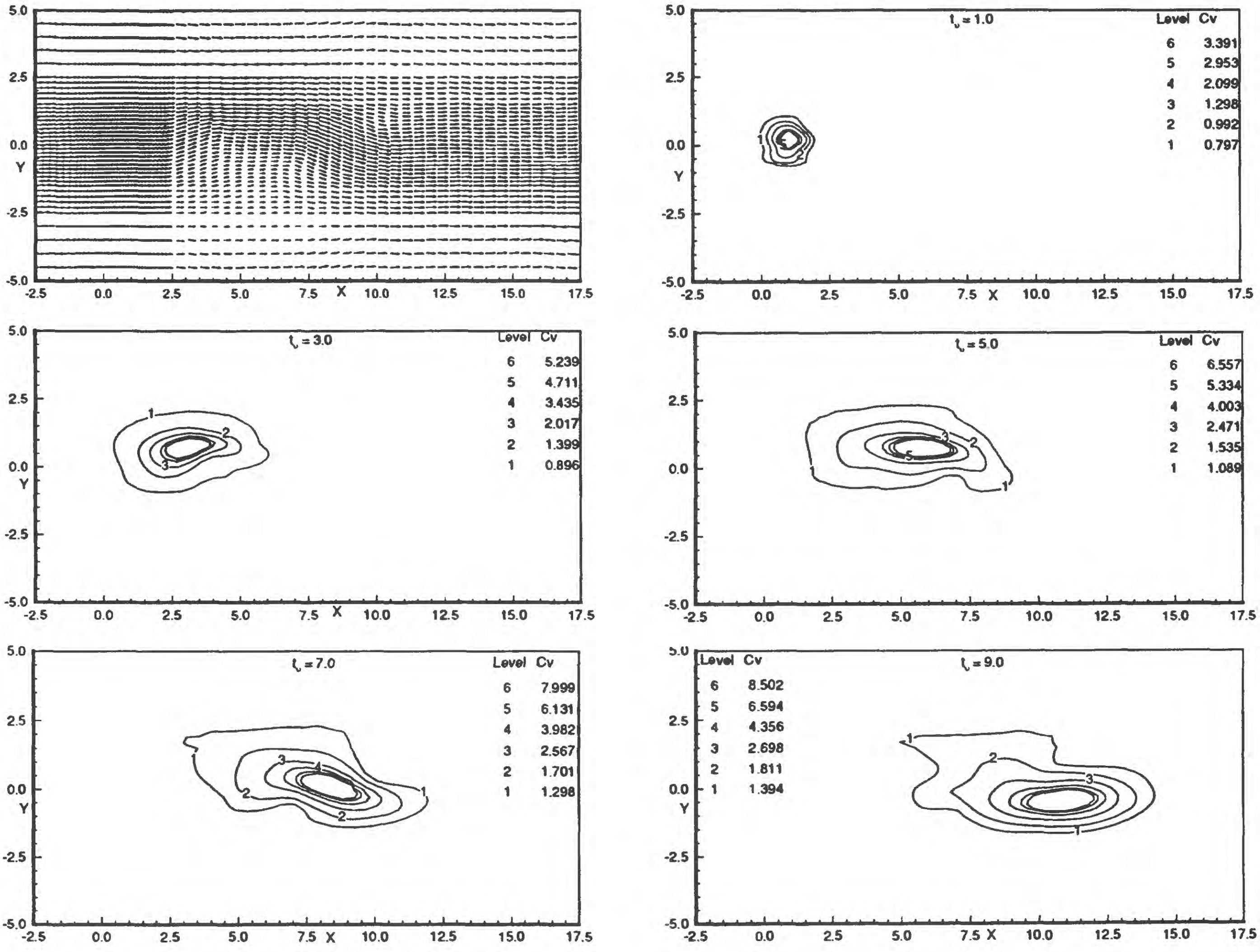

Figure 47. Conditional mean velocity (upper left) and lower bound concentration coefficient of variation (Cv) at various dimensionless times due to an instantaneous point source (conditional on 5 x 5 Y' data). See text.

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VAPOR-PHASE TRANSPORT MODELING OF VOLATILE RADIONUCLIDES

By Michael A. Celia

Introduction

The unsaturated zone provides the link between the land surface and the saturated ground-water zone. It is characterized by the presence of both air and water in the void space of the porous medium. Each of these fluids has its own properties, and both fluids respond to dynamic forcings such as infiltration of water. Air-phase dynamics in the unsaturated zone provide an important coupling to atmospheric models, while water-phase dynamics can provide an important coupling to the deeper ground-water flow system. In addition, interphase mass transfer of water (vapor) and contaminants is important to both water budgets and to contaminant transport.

When air-phase dynamics are included in a mathematical description of the unsaturated zone, the system becomes quite complex. In the most general case, equations must be written for each fluid phase, and material-dependent properties such as relative permeability functions must be defined for each fluid phase. This leads to a system of coupled partial differential equations that are highly nonlinear. Solution of these equations provides a detailed description of the response of the system to various natural or imposed forcings. Subsequent solution of the associated contaminant transport equations provides a description of contaminant movement.

Practical implementation of these general multiphase flow and transport equations is difficult because of the data requirements and because of large computational requirements. This paper presents a general description of air-phase dynamics, then examines issues related to data requirements and to possible simplifications that can be used in the analysis of two-phase unsaturated flow and transport systems. Simplifications include reduction of dimensionality, explicit identification of time scales, and modified mathematical and numerical procedures.

Air-Phase Dynamics

Richards' equation is often used to describe the movement of water in unsaturated soils. In Richards' approximation, the air-phase equation is ignored by assuming that the air remains at atmospheric pressure everywhere in the soil column. This is usually a reasonable assumption in the absence of water ponding at the surface (see, for example, Celia and Binning, 1992a; Touma and Vauclin, 1985). The reason that Richards' equation works well to describe water movement is that the viscosity of air is orders of magnitude less than the viscosity of water. This gives air a very high "mobility," which means that only small pressure gradients are required to induce significant flows of air. Because significant quantities of air can flow with only small pressure gradients, as long as the air maintains a connected path to the land surface (where the pressure is atmospheric), the pressure within the soil will not deviate much from atmospheric pressure. Thus an assumption of air pressure close to atmospheric is usually a good one. As an example, consider the system illustrated in figure 48. In that figure, water is infiltrating along a strip at the land surface into a heterogeneous sand and gravel outwash (characterization of the outwash is based on measurements from the U.S. Geological

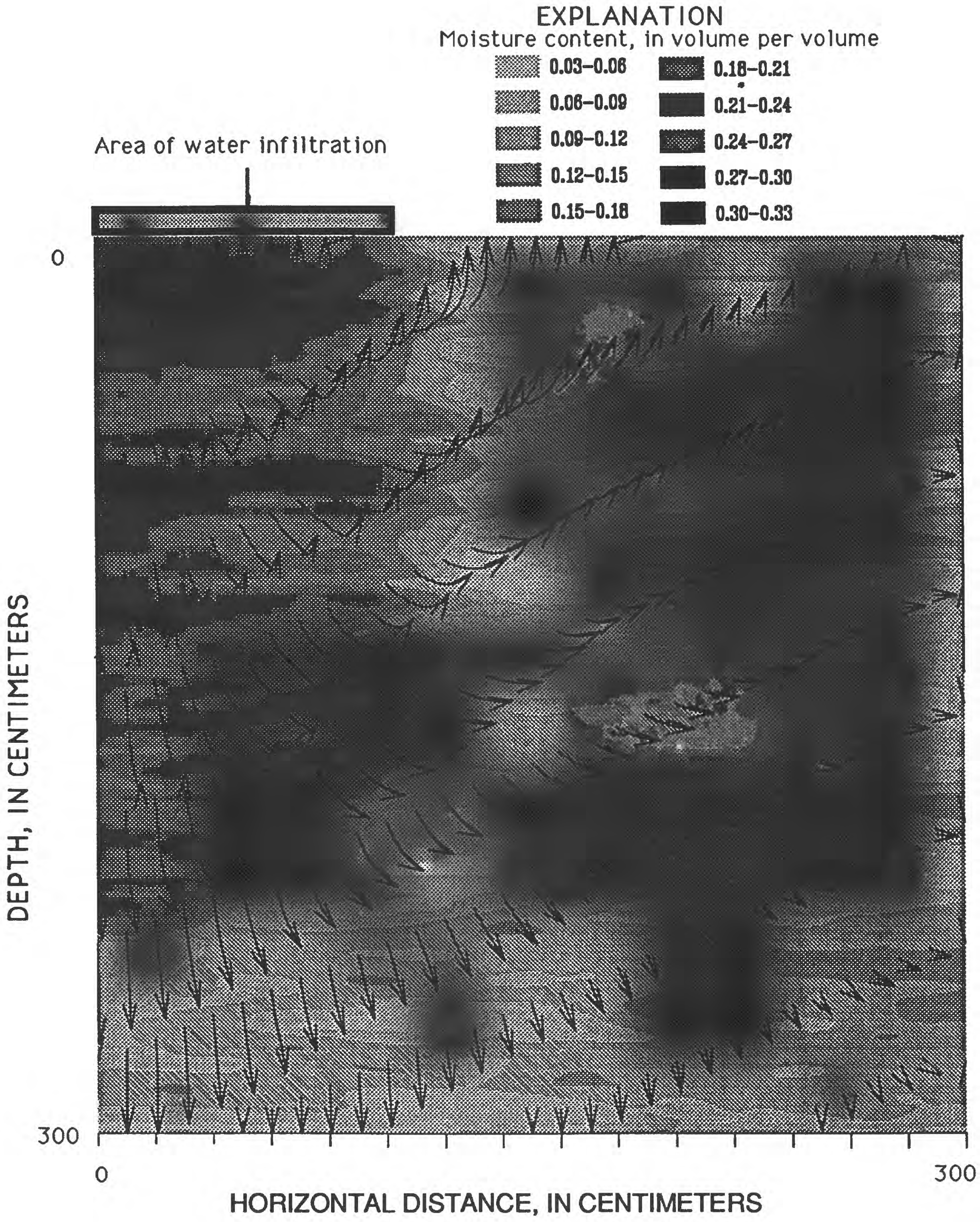

Figure 48. Moisture content profile after 3 hours of infiltration at 7.9 centimeters per hour. Area of infiltration shown by bar at upper left. Arrows indicate transectories of air particles.

Survey Cape Cod Research site). The grayscale represents water content, while the super-imposed arrows show trajectories of air particles. Air is moving throughout the domain, and a significant amount of air is moving upward. This demonstrates that during infiltration events, advective air-phase motion will produce a pulse of air exiting the soil column to the atmosphere. This can lead to pulses of elevated contaminant fluxes to the atmosphere if a volatile contaminant is present.

It may be important to recognize that the assumption of air pressure remaining at essentially atmospheric does not mean that the air phase is stagnant, as has been claimed in a number of publications (see, for example, Bear, 1972, 1979; Chen and others, 1992, among many others). Indeed, whenever the water content changes in time, there will, in general, be flow of both the water and the air phases. While the air-phase flow usually does not have a significant effect on the water movement (which is why Richards' equation is successful for modeling water flow), air-phase flows may have a significant influence on contaminant transport when the contaminant is volatile. Therefore transport analyses for radionuclides such as ^{14}C or ^{3}H may require consideration of air-phase dynamics.

Data Requirements

When analyzing the unsaturated zone as a fully-coupled, two-phase system, data requirements must be taken into consideration. There are three main physical properties that must be identified in these systems: (1) the functional relationship between moisture content and capillary pressure (where capillary pressure is defined as the difference between the air and water pressures),
(2) the functional relationship between the water-phase permeability and the moisture content, and (3) the functional relationship between the air-phase permeability and the moisture content. All three of these functional relationships are nonlinear and hysteretic, and measurements of the relationships are difficult and very time-consuming. This means that site characterization becomes a very difficult issue.

In addition to the hydraulic properties, transport properties are also required. For example, effective diffusion coefficients and dispersivities must be provided for each fluid phase. In addition, behaviors at phase boundaries must be described, including adsorption onto solid surfaces and mass exchange between the fluids. Choices between kinetic or equilibrium partitioning may also be important. These parameterizations will be dependent on the contaminant under consideration.

Finally, as in all porous media systems, the issue of spatial variability must be mentioned. Each of the functional relationships described above will vary with spatial location. Because there are a large number of parameters that need to be identified, questions of cross-correlation between some or all of these parameters can also be raised. The ultimate question is how much detail is necessary for "adequate" characterization of a site, and what sorts of engineering judgements can be made to render the system tractable.

Dimensionality And Scales

A detailed three-dimensional description of a field site is a practical impossibility. Therefore, some reduction of model complexity may be necessary for the system to be tractable. Because unsaturated systems are often driven by forcings applied at the land surface (rainfall, evaporation), one might argue that the areal correlation of these land-surface events is typically large compared to the area associated with an unsaturated-zone contamination event. If this is the case, then a reduction to a one-dimensional vertical description may be reasonable. Of course, other features of the problem, including design features at specific disposal facilities, can make multi-dimensional flow and transport important even in the presence of relatively uniform forcings at the surface.

If a reduction in dimensionality is applied, or if parameters need to be defined in a multi-dimensional representation at scales large relative to the scale of measurements, then some "effective" parameters must be defined. This task may be viewed in a stochastic sense (for example, see Gelhar, 1993), or it may be viewed in a computational sense (for example, see Ferrand and Celia, 1992; Celia and others, 1993). Either way, for cases of multiphase flow, definition of effective parameters remains a difficult issue.

While length scales are often discussed in the context of flow in porous media, time scales are often ignored. When studying air-water systems, time scale becomes quite important because different mechanisms can dominate at different time scales. For example, during a rainstorm, there are significant dynamics in both fluid phases, with water infiltrating and air escaping toward the land surface. If the system is resolved to a time scale that respects each individual rain event, then advective fluxes in both phases may be important and need to be considered explicitly. However, if long-term averages are used (for example, average annual precipitation), then short-time advective movement would need to be filtered into a larger mixing coefficient. Because of the high degree of nonlinearity in unsaturated flow systems, time-averaging can be a difficult issue. One question of practical significance is the relative importance of (short-term) advective fluxes of air-phase contaminants at the land surface versus (long-term) diffusive fluxes.

Mathematical And Computational Issues

Ultimately, the conceptual picture of the unsaturated zone must be translated into mathematics, and the resulting equations must be solved. From the mathematical point of view, one may ask about the best way to represent the unsaturated system. For the focus on contaminant transport in the air phase, air-phase dynamics may be estimated in several ways. The standard coupled flow equations (one for water, one for air) may be solved simultaneously, as described in Celia and Binning (1992a). Contaminant transport in each phase can then be determined from the velocity fields for each phase. While computationally robust and mass-conserving numerical procedures can be used (Celia and Binning, 1992a), this approach still requires significant computational effort.

Two alternatives to the standard approach of Celia and Binning (1992a) may be considered. Each of these approaches has computational advantages over the standard approach. First, because of the high mobility of the air phase and the observation that Richards' equation is usually adequate to describe the movement of water, air-phase dynamics may be estimated by a post-processing of the Richards' equation solution. This is accomplished by taking the local change in moisture content with time from the Richards' equation solution and using it as a known forcing function in the air-phase equation. This allows the air pressure distribution to be solved without iteration, leading directly to air-phase velocities via Darcy's law. Numerical experiments indicate that this provides solutions within a few percent of the fully coupled solutions, as long as Richards' assumption is valid.

A second approach involves the use of fractional flow functions to determine phase saturations. Details are provided in Celia and Binning (1992b). Example calculations for one-dimensional systems indicate that one to two orders of magnitude increase in computational efficiency can be achieved using this approach, relative to the standard two-pressure approach. This approach seems very promising, although a number of details remain to be worked out before it can be applied to general problems of practical importance.

Conclusion

Simulation of volatile contaminant transport in unsaturated soils is complicated by many factors. These include data requirements and site characterization, identification of appropriate length and time scales, and underlying computational requirements.

Significant air-phase dynamics can occur over short time scales. This influences the flux of contaminants to the atmosphere at the land surface. Air-phase dynamics should be included explicitly in short-time-scale models and implicitly, through modified mixing coefficients, in long-time-scale models.

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PROCESSES AFFECTING ^{14}C TRANSFER FROM BURIED LOW-LEVEL RADIOACTIVE WASTES TO THE ATMOSPHERE AND TO LOCAL VEGETATION

By Ted McConnaughey

Introduction

Physical, climatic, and biogeochemical factors affect the migration of ^{14}C from buried low-level radioactive wastes, and its incorporation into surface biota. Studies by the

USGS, in cooperation with the Department of Energy and the State of New York, illustrate some of these processes at the low-level waste disposal site near West Valley, New York.

Background

A combination of factors have made ^{14}C an isotope of major concern within the low-level waste arena. Carbon-14 is fairly abundant in the waste stream, has a relatively long half life (5,730 yr), is rapidly incorporated into organisms, and is highly mobile in gaseous and dissolved species. Over long time periods, ^{14}C, has been identified as one of the radionuclides which will contribute most to the exposure of large populations (Organization for Economic Cooperation and Development/Nuclear Energy Agency, 1980). Despite the interest in ^{14}C, relatively little is known about how it moves at existing low-level waste disposal sites, or is likely to behave in future disposal sites.

Site and design specific issues will become more important as individual States or compacts of States implement their own low-level waste disposal solutions, as mandated by the Low-Level Radioactive Waste Policy Act of 1980 and its 1985 amendments. Performance assessment has focused on "generic sites," which lack characteristics, such as soil desiccation cracks, important at specific sites.

Performance assessment has furthermore emphasized hydrologic factors which affect downward solute movement, over factors which affect the movement of trench and soil gasses. The latter often move predominantly upward, due to a combination of gas generation within the wastes, barometric pumping, and greater upward permeability. Finally, performance assessment has tended to use "concentration ratios," which predict how isotopes will be transferred from soils to plants to animals. Relatively little is known about how much carbon uptake or exchange occurs within plant roots, but most plant carbon uptake is of course through the leaves. For such reasons, ^{14}C presents some special and largely unresolved regulatory issues.

Buried Wastes at West Valley

Twelve trenches were excavated to depths of about 20 ft into silty clays near the Western New York Nuclear Service Center, and filled with low-level radioactive wastes between 1963 and 1975. These wastes were derived from the adjacent nuclear fuel reprocessing site and outside sources. The trenches were covered with excavated materials, and these covers later augmented while retaining only approximate indications of where the trenches actually lay. Trench contents were later established through chemical and radiological surveys, and from partial reconstructions based on shipping records (for example, see Prudic, 1986).

Downward isotope migration through unfractured, unweathered clay appears to be minimal both in the low-level waste disposal area (Prudic, 1986) and in the adjacent NRC disposal area (Kool and Wu, 1991). The trench covers exhibit considerably higher permeability to both water and gases however, despite continuing efforts to seal them. Trench water levels increase immediately following specific rainfall events, and pumping has been required almost since the site opened to remove infiltrating waters and prevent overflow of trench leachates. Infiltration and gas exchange occur largely through cracks caused by waste settling and summertime desiccation of the clays. These cracks are often easily visible, usually running along the trenches near the base of the sculpted trench cap.

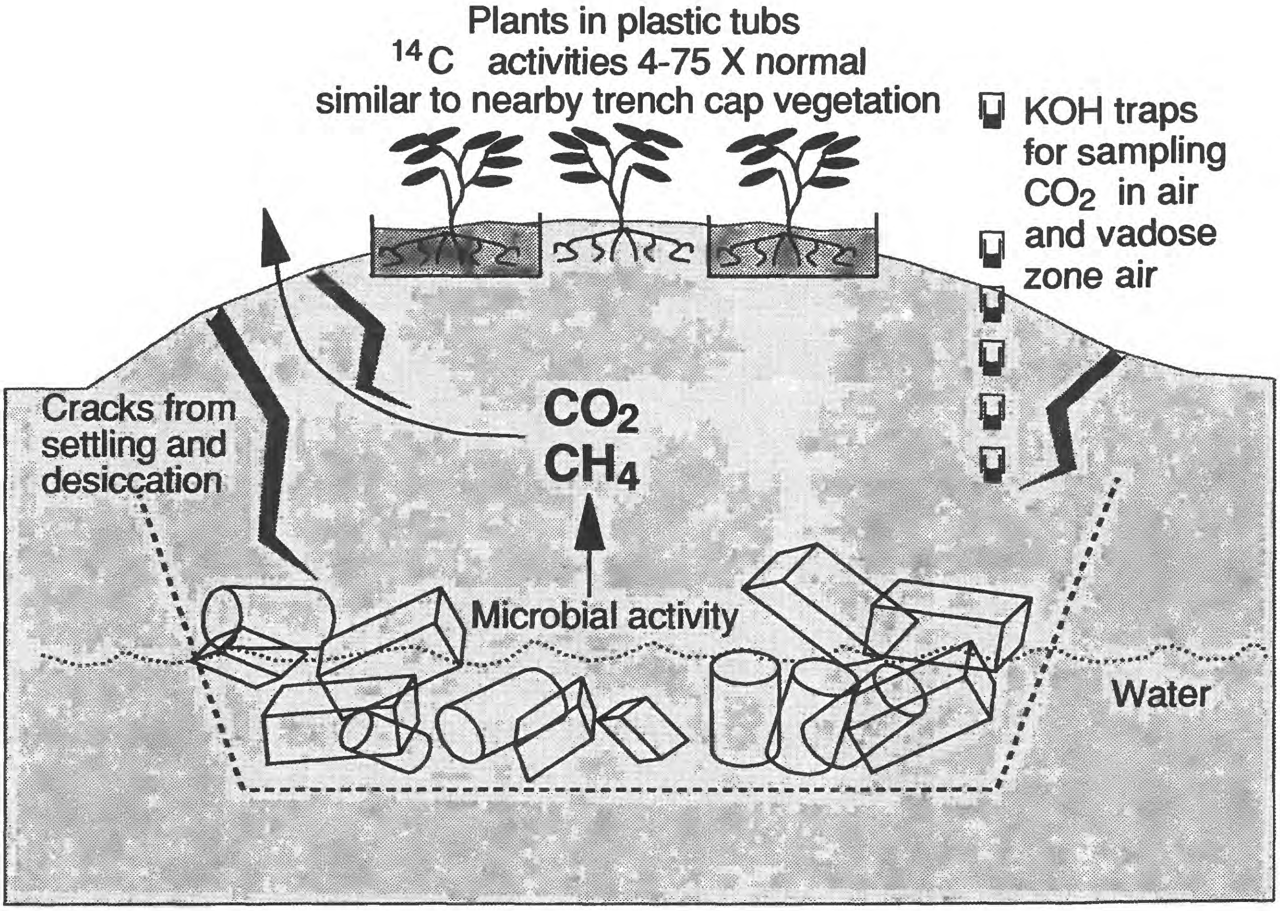

Figure 49. Complexities involved with ^{14}C transfer from buried radioactive wastes to surface vegetation and animals. Aspects of particular interest include biodegradation of the wastes, migration of ^{14}C bearing gases and solutes through surrounding materials, and transfer to aquifers, the atmosphere, and surface vegetation.

Trench Gas Generation and Movement

Biodegradation of buried wastes proceeds much as it would at any landfill, affected by waste type and packaging, permeability of the overlying wastes type and packaging, permeability of the overlying wastes and soils, temperature, and water (for example, see Kunz, 1982; Matuszek and Robinson, 1983). Low-level wastes consist largely of industrial materials and packaging degrade relatively slowly. Redox state affects degradation rates and products. Oxidizing conditions prevail when air readily penetrates to the waste, and carbon dioxide is then the main product. Reducing conditions are likely if soil permeabilities are low, and especially if the wastes are covered with water. Reducing conditions may also prevail within isolated pockets, even when the waste conditions are generally oxidizing Decomposition under reducing conditions produces methane as well as carbon dioxide, and is likely to be slower.

Carbon dioxide and methane concentrations have been measured in vertical soil sampling profiles, and gas fluxes between soils and the atmosphere have been estimated using static flux chambers placed over the trench caps at night. Net upward fluxes of carbon dioxide and methane are generally observed using flux chambers. Soil methane concentrations were considerably higher during 1992, which was unusually cool and wet, than in 1991, which was unusually dry. These differences reflect changes in the rates of production and consumption, and rates of gas exchange with the atmosphere, which are controlled largely by soil hydrology. Methane concentrations generally increase with depth, while subsurface carbon dioxide maxima are sometimes observed. However, these observations probably bear more on normal soil processes than on gas escape from buried wastes.

Carbon dioxide and methane generated during waste decomposition move upward through unsaturated soils and cracks by diffusion and by advection, driven by gas generation within the wastes, rising water tables, and falling barometric pressures. Estimates of trench cap air permeability vary considerably, as might be expected in a fracture flow system of varying expression. Settling and desiccation cracks tend to open during the summer, resulting in seasonal venting of trench gases. Once ^{14}C enters the gas phase, it appears to escape rapidly to the atmosphere.

Precipitation, sorbtion, and exchange processes could potentially retard $^{14}CO_2$ movement through the soils, but rapid gas transport through the fracture-flow network, and the low concentration of carbonates in the soils, suggest that retardation is minimal at West Valley. Microbial oxidation of methane to carbon dioxide probably does reduce the releases of ^{14}C bearing methane, although net isotope release would not be strongly affected.

Carbon dioxide levels within the vegetation canopy (generally about 20 cm thick) range widely. Values both below and above atmospheric carbon dioxide levels have been observed, reflecting uptake by local vegetation, and carbon dioxide release from soils and vegetation. Because the atmospheric boundary layer is chemically distinct from the overlying atmosphere, some boundary layer ^{14}C enrichment would be expected. Analyses are still pending for carbon dioxide collected at various heights above ground level, and various depths below the soil surface.

Surface vegetation at West Valley generally contains two to five times higher ^{14}C activities than would be expected off site. Carbon-14 activities near the north end of trench 5 reach 50 times modern, and the large isotope differential there (compared to the atmosphere) has been exploited to learn more about isotope transfer into surface vegetation. Variation between species or between different parts of individual plants appears to be relatively minor. Roots and shoots, for example, exhibit similar ^{14}C activities, suggesting that the carbon pools within a plant are reasonably well mixed. Plants growing on the trench caps were compared with plants grown inside plastic tubs, containing soil from off site, emplaced near the top of the trench cap. Carbon-14 activities were similar, suggesting that most of ^{14}C in these plants was derived from local atmosphere. These trench garden experiments suggest that the atmospheric boundary layer experiences significant local ^{14}C enrichments.

Lessons From West Valley

Subgrade burial under moist climates invites certain problems. Waste compaction and decomposition leaves the trench cap unsupported, causing structural failures and far higher permeabilities than would occur for undisturbed soils. Infiltrating waters overflow unless pumped out, and require treatment. Burial within an impermeable geological medium therefore does not ensure isolation of water soluble wastes.

Waste compaction before burial and mounding of trench caps to ensure runoff are possible mitigatory measures. Experiments are in progress at West Valley to increase evapotranspiration and decrease infiltration.

Gases resulting from decomposition of organic materials potentially carry away most ^{14}C long before a single half life (5,730 yr) of the isotope has elapsed. Decomposition can potentially be inhibited by preventing aeration, and addition of limestone to trench covers might provide a carbon reservoir for exchange with ^{14}C containing carbon dioxide, delaying release to the general environment.

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WATER-VAPOR MOVEMENT THROUGH UNSATURATED ALLUVIUM IN AMARGOSA DESERT NEAR BEATTY, NEVADA—CURRENT UNDERSTANDING AND CONTINUING STUDIES

By David E. Prudic

Introduction

Disposal of low-level radioactive wastes has been a concern since the 1950's. These wastes commonly are buried in shallow trenches (Fischer, 1986, p. 2). Water infiltrating into the trenches is considered the principal process by which contaminants are transported away from the buried wastes, although gaseous transport in some areas may be important. Arid regions in the western United States have been suggested as places that could provide safe containment of the wastes, because little or no water would infiltrate into the trenches (Richardson, 1962), and because thick unsaturated zones would slow contaminant movement. Although burial in arid regions may greatly reduce the amount of water coming in contact with the waste and consequently may provide long-term containment, insufficient data are available on the effectiveness of burial in such regions. Of particular interest is the potential for contaminant movement, either as liquid or vapor, through unsaturated sediments to land surface or to underlying ground water.

Since 1962, low-level radioactive wastes have been buried at a disposal facility in the Amargosa Desert, about 17 km south of Beatty, Nevada (fig. 50). This facility is in one of the most arid regions of the United States. Annual precipitation at the disposal facility averaged 82 mm for 1985-92; the minimum was 14 mm, recorded for 1989 (Wood and Andraski, 1992, p. 12).

Investigations to determine the hydrogeology, water movement, and potential for contaminant movement at the facility began in 1976. Results from an initial study indicated that a potential exists for deep percolation of infiltrated water at the burial site (Nichols, 1987), assuming that the only water loss is by evaporation because the trenches are kept clear of vegetation. Results from a subsequent study of water movement beneath an undisturbed, vegetated site indicate that percolation of infiltrated water may be limited to the uppermost 9 m of sediments, on the basis of water potentials, subsurface temperatures, water content, and sodium chloride content of the sediments (Fischer, 1992, p. 1). One objective of a third study that began in 1987 is to determine how the typical procedure of burying wastes alters water movement and affects the potential for deep percolation of infiltrated water (Andraski, these proceedings). In addition to these studies, a fourth began in 1992 to determine the importance of vapor movement through the unsaturated zone.

The purpose of this paper is to summarize the current understanding of water movement (as liquid and vapor) through the upper 13 m of unsaturated sediments beneath the undisturbed, vegetated site and to present plans for determining the importance of water-vapor movement from land surface to the water table.

Stratigraphy of Sediments

The study site is outside the southwest corner of the waste-disposal facility; about 3 km east of the main channel of the Amargosa River (fig. 50). The surficial deposits at the site are alluvial sheet sand deposits (Swadley and Parrish, 1988). These deposits are prevalent in the vicinity of the waste-disposal facility and consist mostly of silt and sand with minor gravel. The deposits generally have a smooth, undissected surface, which is covered by a thin layer of gravel (lag pavement). Beneath the sand and extending to a depth of about 30 m are fluvial deposits associated with down-valley movement of surface water (Nichols, 1987, p. 8-9); these sediments include channel deposits of sand and gravel separated by interchannel deposits of sand and gravel containing considerable silt and clay. Below a depth of 30 m, debris-flow and lacustrine deposits are more common. A clay unit, found at depths from 70 to 90 m (Fischer, 1992, p. 6), is laterally extensive beneath the waste-disposal facility. The water table is 85 to 115 m below land surface (Fischer, 1992, p. 12) and is generally beneath the extensive clay unit.

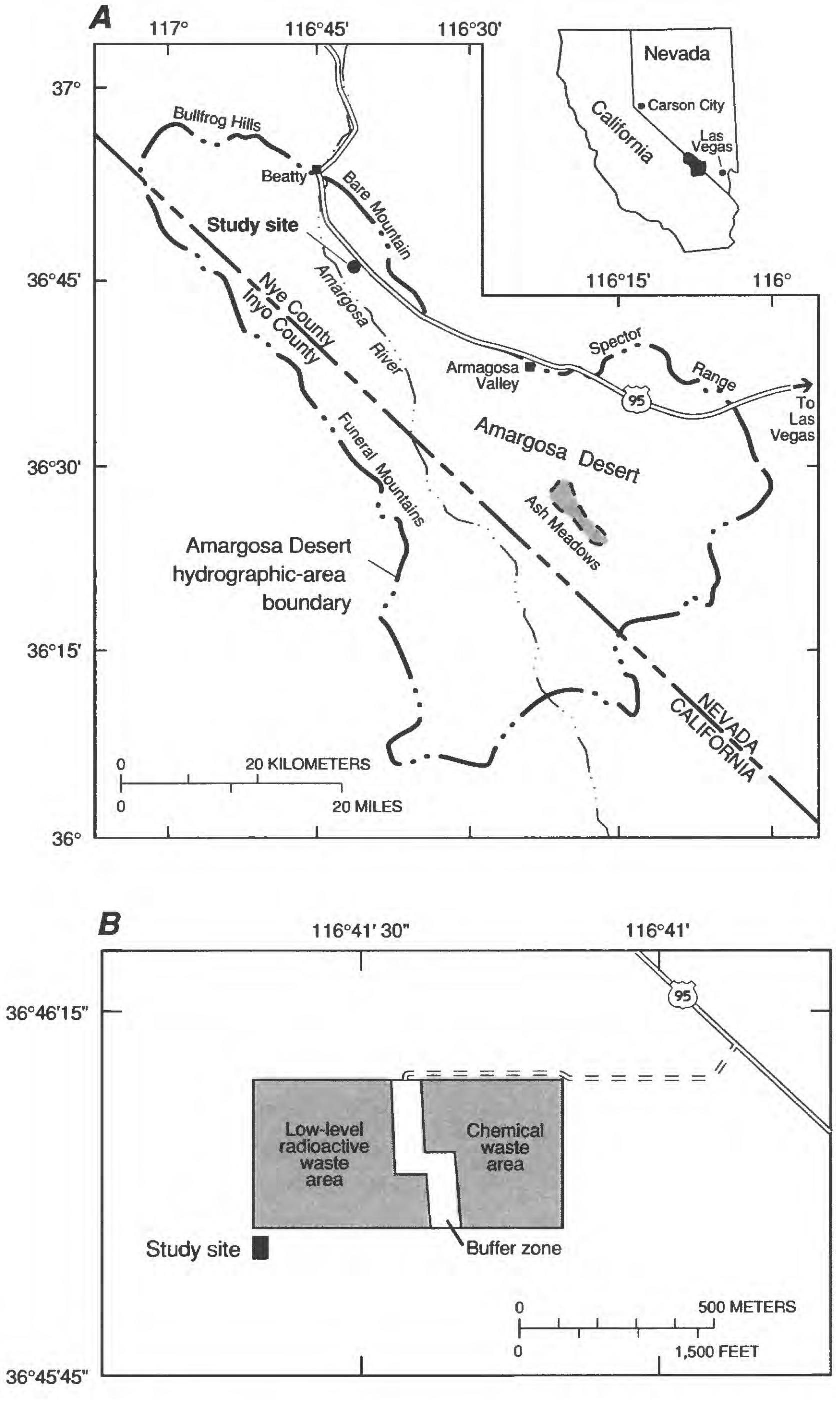

Figure 50. Location of (*A*) waste-disposal facility in Amargosa Desert and (*B*) study site in relation to disposal facility (from Fischer, 1992, fig.1).

Shaft Installation

A 13.7-m-deep monitoring shaft was installed at the southwest corner of the disposal facility in 1983 to study water movement through undisturbed sediments (Fischer, 1992, p. 15). The shaft has 33 access ports; three ports every meter between the depths of 3 and 13 m that are oriented toward an area undisturbed by the installation of the shaft (fig. 51). Between 1984 and 1986, 17 horizontal holes were drilled 3 to 4 m outward from selected access ports in the shaft using a blast hole drill. Thermocouple psychrometers, used to determine water potentials and subsurface temperature, were inserted through 2.5-cm diameter pipes placed in the horizontal holes. The annular space between the pipe and hole was sealed with a polyurethane foam. Thermocouple psychrometers also were placed in a nearby borehole drilled in 1986 (Fischer, 1992, p. 18). The thermocouple psychrometers have been monitored in the shaft and borehole since 1986. Water content of the sediments has been monitored routinely in three cased boreholes surrounding the undisturbed site (fig. 51) using a neutron-moisture probe. These data, along with physical properties determined from sediment samples and soluble salts from soil-water extracts, form the basis for the current understanding of water movement beneath an undisturbed site.

Current Understanding of Water Movement

The upper 13 m of unsaturated sediments beneath the undisturbed site can be divided into three zones: upper, middle, and lower. Water movement in the upper zone, which extends from land surface to a depth of about 2 m, is both upward and downward. This zone includes the surficial alluvial-sheet deposits of sand and an underlying coarse-sand-and-gravel unit. Water potentials in the finer grained surficial sand are generally too low to induce liquid flow through the coarser sand and gravel; under normal conditions, the coarser deposits act as a barrier to downward liquid flow. Water-content changes have not been observed below the depth of about 1 m (fig. 52), which is near the base of the surficial sand. Within the upper meter, rapid changes in water content, water potential, and temperature have been observed in response to precipitation, and to diurnal air-temperature fluctuations.

Water movement in the middle zone, which extends from a depth of about 2 m to 9 m, also is both upward and downward. This zone includes layers of poorly sorted sand and gravel with silt and clay, separated by layers of coarse sand and gravel. Water content in this zone is unchanging, whereas both water potentials and temperatures change seasonally (fig. 52), producing seasonal reversals in the water-potential and vapor-density gradients.

Water movement in the lower zone, which extends from a depth of about 9 m to at least 13 m, is generally upward. This zone includes deposits similar to those of the middle zone. Water content in this zone is unchanging, and water potentials and temperatures exhibit only minor seasonal changes (fig. 52). Water-potential gradients are consistently upward, suggesting that liquid water flow is upward also. Small downward vapor-density gradients are calculated seasonally to a depth of 12 m, suggesting that vapor flow may extend deeper into the sediments than liquid flow. In this zone, estimates of liquid-water flux range from 0.00004 to 40 mm/yr (Fischer, 1992, p. 38). The range is due to large uncertainties in the value of unsaturated hydraulic conductivity. Estimates of upward water-vapor flux, assuming vapor diffusion, are about 0.07 to 0.18 mm/yr (Fischer, 1992, p. 42).

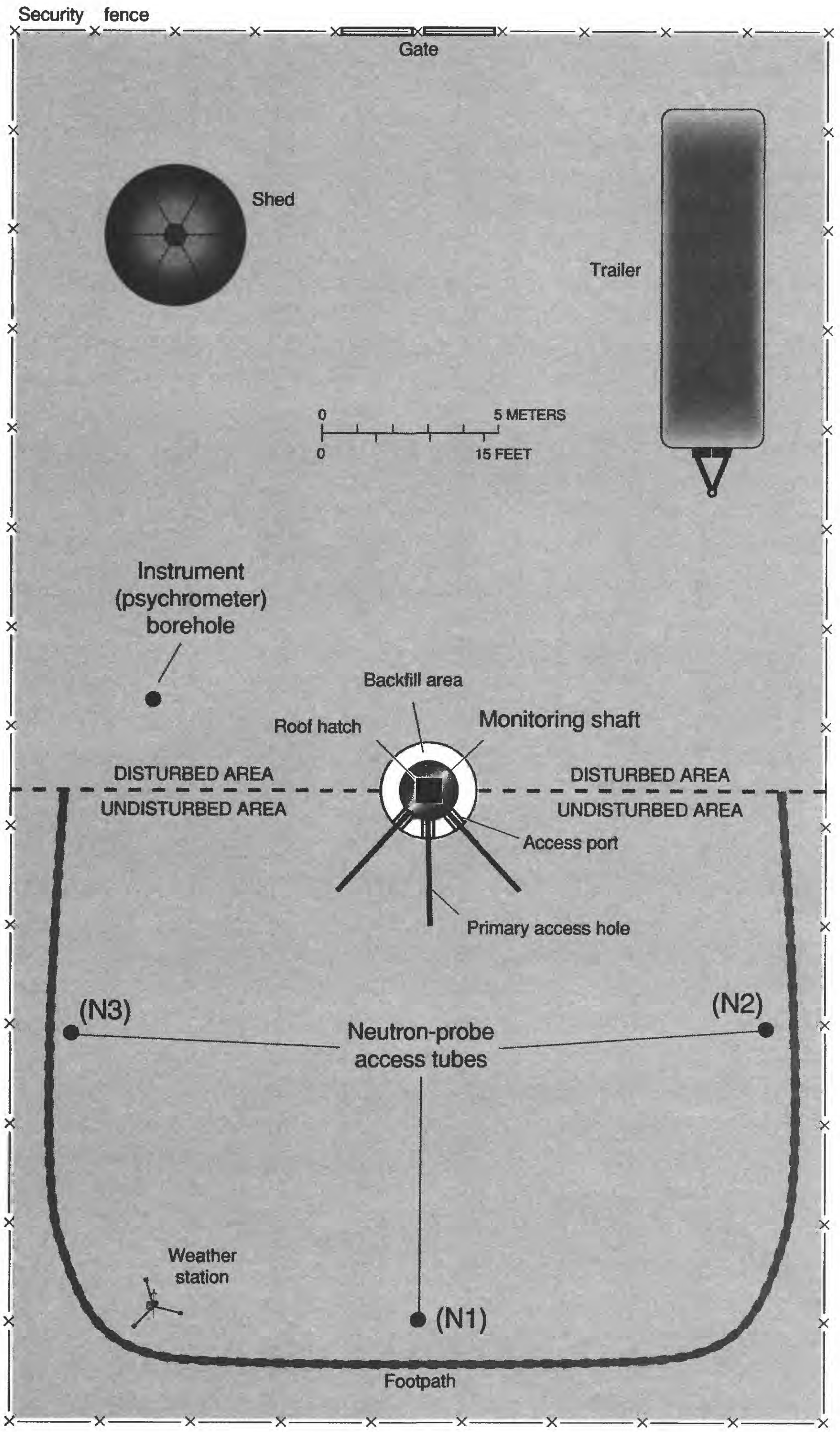

Figure 51. Location of monitoring shaft, neutron-probe access tubes, and instrument borehole at study site (from Fischer, 1992, fig. 2)

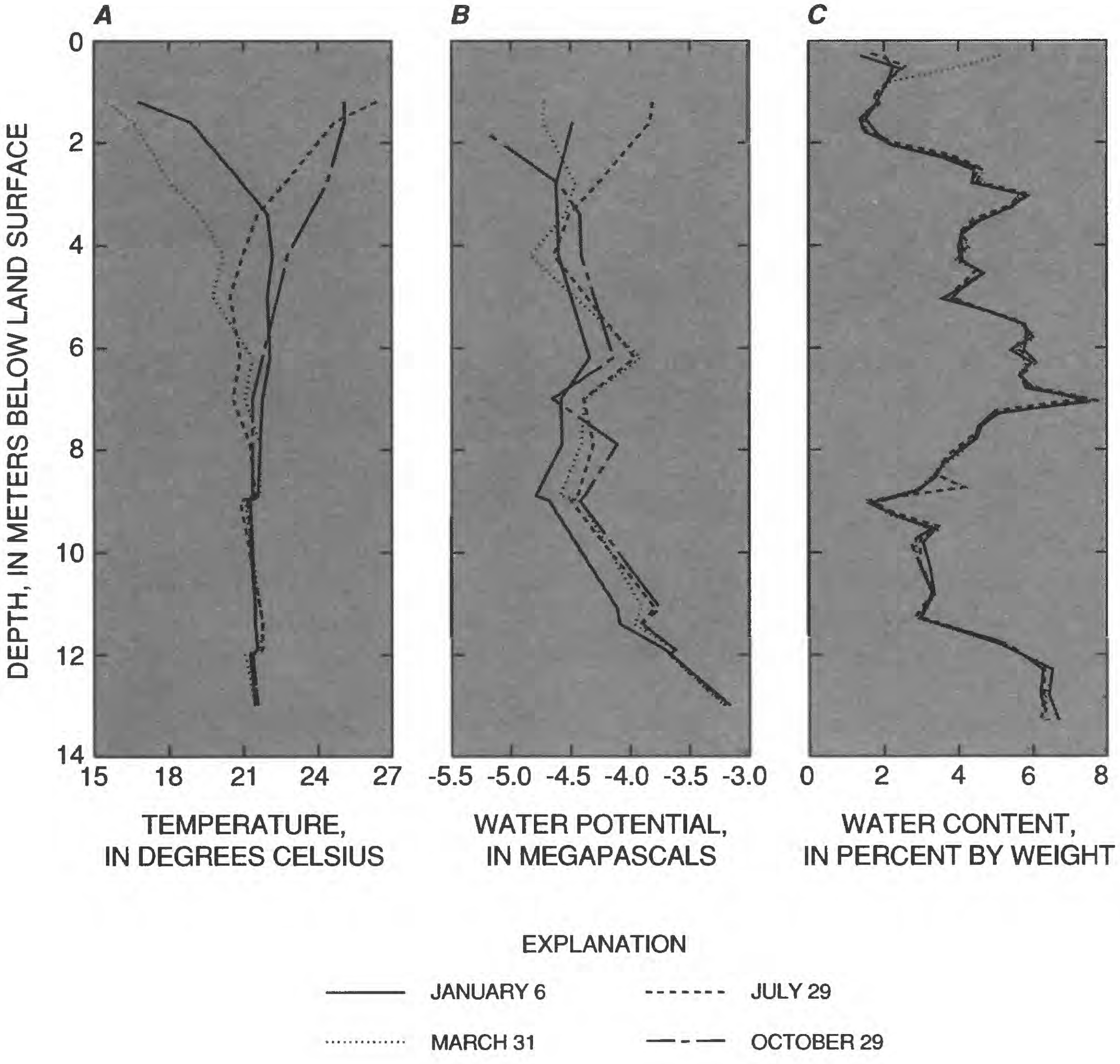

Figure 52. Profiles of temperature, water potential, and water content in the upper 13 meters of unsaturated sediments at study site for selected dates in 1987 (from Fischer, 1992, fig. 21).

The distribution of anions in soil-water extracts provides additional evidence that downward percolation is limited to the upper 9 m of the sediments. The distribution of chloride in the sediment profile can be used to estimate recharge rates to ground water because chloride salts are soluble in water and often are assumed to move at the rate of water (Allison and Hughes, 1983). The distribution of chloride in the sediments was determined from core samples collected in the nearby instrument borehole (fig. 51) (Fouty, 1989, chap. 3; Fischer, 1992, p. 27). Chloride concentrations peak between the depths of 2 and 4 m and decrease to low concentrations at a depth of about 10 m. On the basis of this distribution, Fouty (1989, p. 14) concluded that downward flow below a depth of 10 m has been minimal or nonexistent for thousands of years. This conclusion is based on the assumptions that the surface is neither aggrading nor degrading, that long-term precipitation ranges from 50 to 175 mm/yr, and that the concentration of chloride in precipitation is 0.5 to 1 mg/L.

Peak concentrations of carbonate and sulfate in soil-water extract of core samples are at shallower depths than that of chloride. Sulfate concentration peaks at a depth of about 125 cm and bicarbonate peaks near land surface. Peak concentrations of bicarbonate coincide with the caliche deposition on the underside of larger clasts. The sequence of carbonate, followed by sulfate, then chloride can be explained by evaporation of percolating precipitation in a manner similar to the evolution of brines in closed basins (Eugster and Jones, 1979).

Plans for Determining Importance of Water-Vapor Movement

In comparatively dry sediments, such as those observed in the upper 13 m at the undisturbed site, temperature gradients may be as important as water-potential (head) gradients to the movement and distribution of fluids (Stallman, 1964, p. E36). In addition, barometric pressure changes have the potential for producing convective air flow through the dry sediments. Computer simulations using a single-component advection-dispersion equation for gas transport indicate that in highly-permeable sediments, atmospheric air can migrate several meters into the subsurface during a typical barometric pressure cycle (Massman and Farrier, 1992). The circulation of atmospheric air into the sediments during periods of increasing pressure may contribute to an overall drying of the surficial deposits.

Estimates of water movement at the undisturbed site are limited to temperature and water-potential gradients in the upper 13 m of sediments. These data, however, suggest that vapor flow may be as important as liquid flow, and that a proper understanding of water movement will require consideration of both phases and the relation between them. Our ability to adequately predict contaminant transport from the buried wastes will depend on our ability to understand the relation between liquid and vapor flow through the naturally dry sediments.

Many questions on water movement at the undisturbed site remain. For example, do the upward water-potential and vapor-density gradients observed below a depth of 9 m continue to the water table? Is liquid flow downward at some unknown depth even though vapor flow is upward? What effects do barometric pressure changes have on the movement of water vapor and other gases in the sediments? How do temperature gradients in the sediments affect the convective flow of water vapor and other gases?

Additional studies are planned to begin answering these questions and to begin understanding the importance of vapor flow at the site. These studies include the following:

- Determine if water-potential and temperature gradients are upward from the water table to a depth of 9 m by drilling test holes, collecting and analyzing core samples for physical, hydraulic, and chemical properties, and installing thermocouple psychrometers.
- Estimate the depth of convective air flow by measuring changes in pneumatic pressure in the sediments as a result of changes in atmospheric pressure and simulate the measured changes using a single-component advection-dispersion equation. Measurements from air piezometers installed by the site operator at the southeast corner of the disposal facility indicate that pneumatic pressures change rapidly in the upper 30 m of sediments in response to changes in atmospheric pressure (fig. 53).

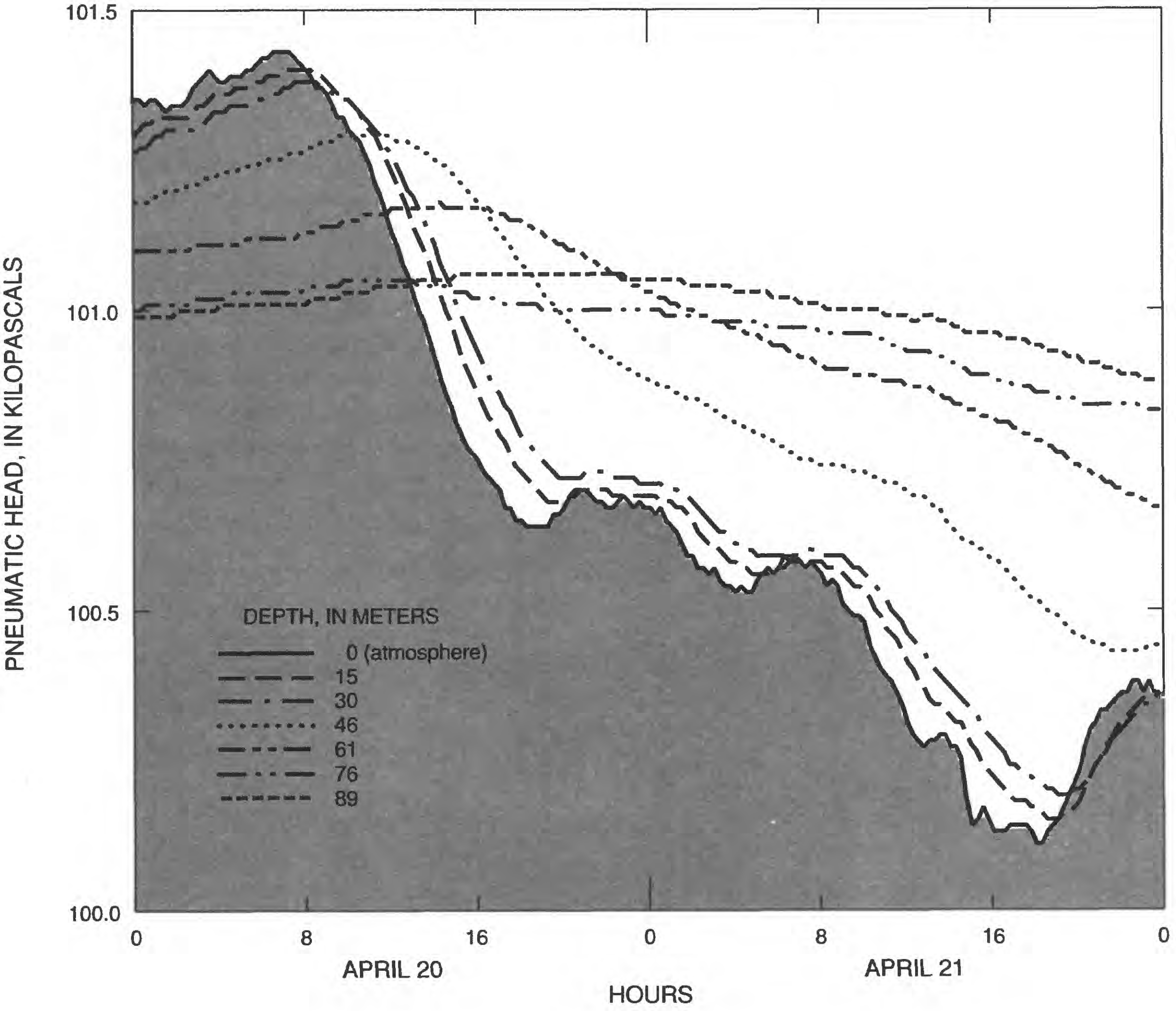

Figure 53. Pneumatic heads measured April 20-21, 1992, at six depths in unsaturated zone near southeast corner of waste-disposal facility.

- Determine the concentration of carbon dioxide, ^{14}C, and other selected gases with depth and through time. Use the distribution of the gases to estimate the rate and depth of atmospheric air circulation in the sediments.

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TRACER TESTS IN SATURATED AND UNSATURATED SAND AND GRAVEL GLACIAL OUTWASH, CAPE COD, MASSACHUSETTS

By Dennis R. LeBlanc

Introduction

The U.S. Geological Survey (USGS) Cape Cod Toxic-Substances Hydrology Research site is located in the northern part of Falmouth, Massachusetts, on Cape Cod (fig. 54). This site is the focus of research on the geologic, hydrologic, chemical, and microbiological processes affecting the movement of contaminants in a sewage plume originating from Otis Air Base. Observations of the distributions of contaminants and bacteria in the plume and field and laboratory experiments have been used to identify and quantify these processes. A summary of research at the Cape Cod site can be found in Garabedian and LeBlanc (1991). The purpose of this paper is to describe the use of tracer experiments to examine the effects of physical and geochemical heterogeneity on fluid flow and solute transport at the site.

Site Description

The study area is on a broad sand and gravel outwash plain formed during the last Pleistocene glacial retreat. The top 30 to 50 m of sediment are composed of stratified, medium to coarse sand with some gravel. The sand and gravel overlies fine sand, silt, and sandy till. These unconsolidated sediments overlie crystalline bedrock. The horizontal hydraulic conductivity of the sand and gravel in the study area ranges from 60 to 90 m/d and is locally as high as 120 m/d (LeBlanc, Garabedian, and others, 1991). The effective porosity of the sand and gravel is about 0.39 (Garabedian and others, 1991).

Ground water in the unconsolidated sediments is unconfined. The water table slopes toward the south at about 1.5 m/km. Recharge to the aquifer from precipitation is about 0.5 m/yr. Estimated rates of average ground-water velocity in the sand and gravel range from 0.2 to 0.6 m/d.

A plume of contaminated ground water has been formed by more than 60 years of disposal of treated sewage onto infiltration beds at Otis Air Base (LeBlanc, 1984a, b). In 1979, the plume was 0.8 to 1.1 km wide, 23 m thick, and more than 3.4 km long. The plume contains elevated concentrations of dissolved solids, boron, chloride, sodium, phosphorus, ammonium, nitrate, detergents, and volatile organic compounds. The distributions of these chemicals in the plume are affected by the physical, chemical, and microbiological processes in the aquifer and by historical variations in the chemical composition of the treated sewage. The microbiological processes are reflected by increased bacterial populations near the infiltration beds (Harvey and others, 1984).

Methods of Study

In the early phase of research at the Cape Cod site, observed distributions of contaminants and bacteria were used to infer the major physical, chemical, and microbiological processes affecting the transport and attenuation of contaminants in the plume, and hypotheses concerning transport were proposed. Among these hypotheses was that physical and geochemical heterogeneity were important factors affecting the fate of contaminants in the aquifer. More recent research has focused on testing the hypotheses and

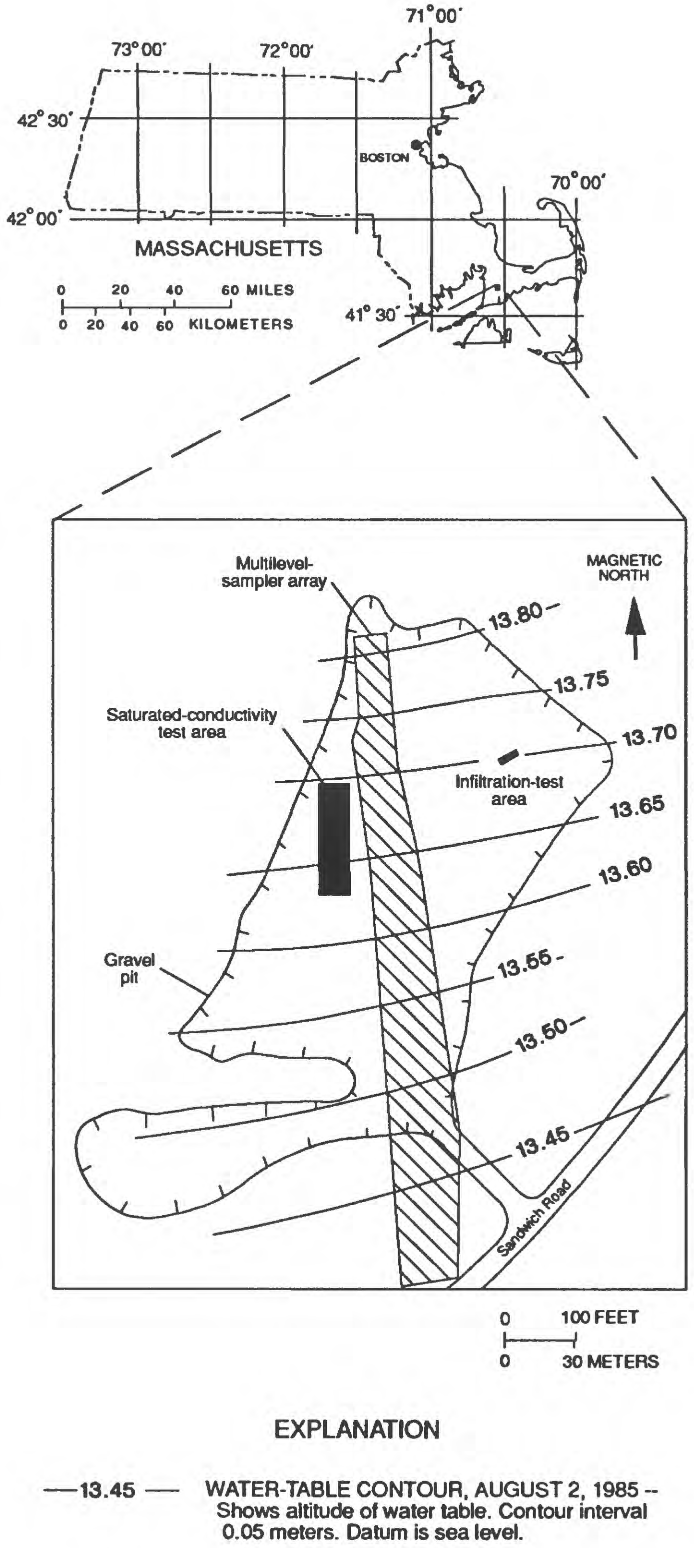

Figure 54. Study area, showing location of multilevel sampler array used in the large-scale natural-gradient tracer test, area where the spatial variability of hydraulic conductivity was measured, and location of the infiltration-experiment test plot.

quantifying the processes affecting contaminant transport and attenuation. These efforts have included large-scale investigations of the sewage plume with specialized sampling methods, intermediate-scale field experiments such as tracer tests with transport distances of 1 to 280 m, and small-scale laboratory experiments such as batch and column tests.

More than thirty tracer tests have been conducted during the past 10 yr as part of research at the Cape Cod site. The tracers used in the Cape Cod experiments include inorganic (bromide, chloride, nitrate, ammonium, lithium, molybdenum, boron, chromium, zinc, nickel, lead, copper, and selenium) and organic (methane, chlorofluoromethane, EDTA, and surfactants) chemicals, bacteria, viruses, and fluorescent microspheres. The tests were conducted with forced- and natural-gradient flow fields over travel distances of 2 to 280 m. These tests are designed to be controlled, in situ experiments for testing specific hypotheses related to transport processes. The tests, although difficult and time-consuming to conduct, help develop an understanding of fluid flow and contaminant transport in the heterogeneous subsurface.

Examples of Tracer Tests

A major research objective at the Cape Cod site has been to relate the dispersion of solutes to the heterogeneity of aquifer hydraulic properties. Two examples of the use of tracer tests--one in the saturated zone and the other in the unsaturated zone-- to address this objective are given in this section.

A direct measure of the dispersion of solutes in the sand and gravel aquifer was obtained by spatial-moments analysis of a large-scale natural-gradient tracer test conducted in the saturated sand and gravel from 1985-87 (LeBlanc, Garabedian, and others, 1991; Garabedian and others, 1991). The nonreactive tracer, bromide, and several reactive tracers were injected as a pulse into three wells in July 1985. The tracers were then monitored in three dimensions as they moved as far as 280 m downgradient through an array of 656 multilevel samplers in an abandoned gravel pit (fig. 54). The bromide cloud moved horizontally at a rate of 0.42 m/d. It also moved downward about 4 m because of density-induced sinking early in the test and accretion of areal recharge from precipitation. After 200 m of transport, the bromide cloud had spread more than 80 m in the direction of flow, but was only 14 m wide and 4 to 6 m thick. A spatial-moments analysis of the bromide distributions at 16 sampling dates during the test indicated that the aquifer dispersivity is about 1.0 m in the direction of flow, about 0.02 m in the transverse horizontal direction, and about 0.002 m in the transverse vertical direction (Garabedian and others, 1991).

Hess and others (1992) estimated macrodispersivity at the Cape Cod site using the statistical properties of the hydraulic-conductivity distribution in the theoretical transport equations of Gelhar and Axness (1983). The statistics were obtained from the analysis of about 1,500 measurements of saturated hydraulic conductivity that were made using borehole-flowmeter measurements and permeameter analyses of cores near the location of the multilevel sampler array (fig. 54). The range of estimated asymptotic longitudinal dispersivity is 0.35 to 0.78 m. This range is similar to the longitudinal dispersivity observed in the large-scale tracer test.

The effects of variations in physical properties of the sand and gravel on unsaturated flow and solute transport were observed in detail during a set of infiltration experiments conducted in 1990-91 in the unsaturated zone (LeBlanc, Randolph, and others, 1991; Celia and others, 1992). Soil-water content, pressure, and solute concentration were measured during infiltration on a test plot 2 m wide and 10 m long adjacent to the multilevel sampler array in the abandoned gravel pit (fig. 54). Instrumentation was installed to a depth of 2 m and included 168 pairs of time-domain reflectometry probes and 112 suction-lysimeter/tensiometers. The 20-m^2 plot was irrigated through sprinkler nozzles set 1.5 m above ground surface. The experiments were divided into two sets. The first set focused on transport of solutes under steady-flow conditions at irrigation rates ranging from 7.9 to 37.0 centimeters per hour. The second set focused on transient water flow during several wetting and drying cycles. After completion of the infiltration experiments, undisturbed cores were collected from the test plot for laboratory analysis of grain size and pressure/saturation relationships, and a trench was dug to a depth of 2.5 m along the centerline of the plot to observe the stratigraphy of the sand and gravel directly.

The data from the infiltration experiments are presently being compiled and analyzed. Preliminary results indicate that physical heterogeneity greatly affects water flow and solute transport in the coarse-grained sand and gravel outwash. Significant variations in flow and solute transport were observed, which are inferred to result from spatial variations in the hydraulic properties of the sand and gravel. Both water and solute appeared to move around a horizontally persistent layer of coarse gravel observed during excavation of the test plot.

Summary

The Cape Cod Toxic-Substances Hydrology Research site is the focus for a number of field research projects studying the physical, chemical, and microbiological processes that affect the transport and attenuation of contaminants in ground water. In the early phase of research at the site, observed distributions of contaminants and bacteria in a plume of sewage-contaminated ground water were used to infer the major processes affecting transport and to propose hypotheses concerning these processes. Among these hypotheses is the importance of physical and geochemical heterogeneity in controlling the fate of contaminants in the sand and gravel outwash. Recent research includes efforts to characterize specific processes using small-scale laboratory experiments, intermediate-scale field tracer tests, and large-scale investigations of the sewage plume with specialized sampling methods.

More than 30 tracer experiments have been run at the Cape Cod site in the saturated and unsaturated zones since 1984. These tests have used inorganic and organic compounds, bacteria, viruses, and fluorescent microspheres as tracers with transport distances of 2 to 280 m. The tracer tests are designed to be controlled, in situ experiments for testing specific hypotheses related to transport processes.

A major research objective at the Cape Cod site has been to relate dispersion of solutes to the heterogeneity of aquifer hydraulic properties. A large-scale natural-gradient tracer test in the saturated zone showed that dispersion of solutes could be related quantitatively to the spatial variability of hydraulic conductivity using theoretical stochastic transport equations. The test also showed that dispersion of solutes transverse to the direction of ground-water flow is limited. A series of infiltration experiments in the unsaturated zone showed that physical heterogeneity greatly affects water flow and solute transport in the coarse, stratified sand and gravel. Observations of water flow and solute transport from tracer studies, although difficult to obtain, help develop an understanding of transport processes in the heterogeneous subsurface.

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DIFFUSION IN SOLUTE TRANSPORT—THREE SCALES OF IMPORTANCE

By Warren W. Wood

Introduction

Solutes in ground water are transported by advection and diffusion. Mass transport by diffusion for a given volume of rock is typically four or five orders of magnitude lower than transport by advection in many aquifer systems. Thus, it has been assumed that solute transport by diffusion plays a minor role in systems in which ground water velocity is large. As a consequence, the diffusion term is usually embedded in the dispersion form of the ground-water-transport equation rather than being identified as a separate mechanism. This paper illustrates that mass transport by diffusion can be important in aquifer systems over a wide range of geologic conditions and time scales. The basic equation controlling the diffusion into geologic material under one dimensional steady state conditions is Fick's First Law

$$q = D\,(dC/dX), \qquad (27)$$

where q is flux $((M/L^2)/T)$; D is diffusion coefficient (L^2/T); C is concentration (M/L^3); and X is distance (L) (L = length; M= mass; T = time, in consistent units).

In this paper the role of diffusion in porous media is evaluated at three different scales, orders of magnitude different in length and time: small-scale (<1 mm) diffusion into and out of individual grains over time in hours to days; intermediate-scale (10 mm-10 cm) diffusion into and out of fractures and surrounding rock matrix over times of months to tens of years; and large-scale (meters) diffusion across geologic formations over times of thousands of years.

Small - Scale Diffusion (<1 mm, hours to days)

Consider a porous media in which a solute is introduced to an aquifer in a measure analogous to that used for a tracer test, industrial spill or disposal of waste. If the individual grains are porous, solutes will diffuse into them in response to the concentration gradient between the interstitial pore space of the aquifer and the interior of the grain. Because diffusion distances into pores are small—less than the radius of the grain--the concentration gradients are large; and because the total surface area of the grains is large, a significant amount of mass transport by diffusion is possible in a short period of time. The process at this scale is illustrated in a glacial outwash deposit on Cape Cod, Massachusetts.

Examination of the aquifer grains by SEM (scanning electron microscopy) illustrate the presence of a honeycomb texture in which parts of the mineral have been removed by weathering (Wood and others, 1990). The probable origin of the honeycomb texture in the feldspar is the differential weathering of the sodium feldspar in a microperthite. X-ray analyses, batch and column tests, and ion-exchange studies (Wood and others, 1990) documented the presence of smectite clay--weathering products in the interior that act as exchange sites for diffusing cations.

Mercury injection studies indicated that internal porosity's of quartz, feldspar and heavy minerals (largely biotite) were approximately 10 percent. This porosity is consistent with porosity observed in the SEM microphotographs and thin sections of grains that had been injected with a fluorescent epoxy.

The role of grain diffusion and interaction is shown dramatically in the shape of the solute plume (fig. 55) resulting from a field-scale tracer test (LeBlanc and others 1991, Garabedian and others 1991). After 236 days

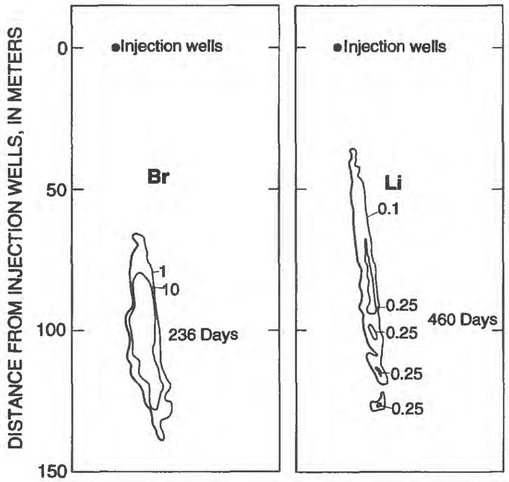

Figure 55. Solute plumes of (*A*a) Br$^-$ and (*B*b) Li$^+$ (lines indicate equal concentrations in mg/L) after transport approximately 140 meters along a ground-water flow path in the Cape Cod aquifer (modified from Wood and others, 1990).

the center of mass of the conservative bromide plume had traveled approximately 100 m. The center of mass of the lithium plume required 460 days to travel the same distance as would be expected of a retarded, reactive solute. Notice in figure 55, the difference in shape of the two solute plumes after they traveled the same distance. Note particularly the long tailing of the Li$^+$ curve and the smaller transverse spreading. We propose that the difference in shape is due to nonequilibrium ion-exchange conditions resulting from Li$^+$ diffusion into the internal grain pores, exchange with the weathering products in the interior, and subsequent diffusion of Li$^+$ out of the grains. Br$^-$ is assumed to diffuse into and out of the grains but is not involved with cation exchange thus the difference in dispersivity between the two ions. There is some indication that Br$^-$ may be excluded from the clay-filled pores and, thus, may have increased the difference in dispersion between the two ions.

Intermediate-Scale Diffusion (10 mm - 10 cm) months to tens of years

Diffusion at this scale is illustrated in a low permeability fractured rock environment in which diffusion occurs from the fracture into the matrix and from the matrix to the fracture. This process is illustrated in a granite at Mirror Lake, Grafton County, New Hampshire.

Consider first the residence time of water in this fracture-dominated system. Of the 100 ground-water samples collected from areal distributed bedrock wells in the upper 150 m of the fractured granite and schist at the Mirror lake site 96 indicate the ground-water residence times are less than 50 yr. This estimate is based in most samples on the fluorocarbons, generated since the late 1940's through the present, and tritium from atmospheric testing of thermonuclear devices in the 1950's and early 1960's that persists to the present.

Evidence for diffusion in this system is observational, experimentally determined, and inferred. Rocks adjacent to fractures in this system exhibit numerous, conspicuous ferric-iron-stained "Liesegang bands" (fig. 56). These bands are believed to have formed in response to the diffusion of ferrous iron, which is generated by weathering of the ubiquitous amphiboles and biotite, toward the fracture in response to a concentration gradient. Oxygen in ground water diffuses from the fracture into the rock matrix, causing precipitation of ferric hydroxide. Paul Hseih (U.S. Geological Survey, oral commun., 1992) has shown, by an analytical solution of the diffusion equation with boundary conditions appropriate for the system, that these ferric hydroxide bands are a consistent response to changing oxygen concentration in the fracture. Further, it can be shown, with the choice of typical effective diffusion coefficients and observed concentrations, that the

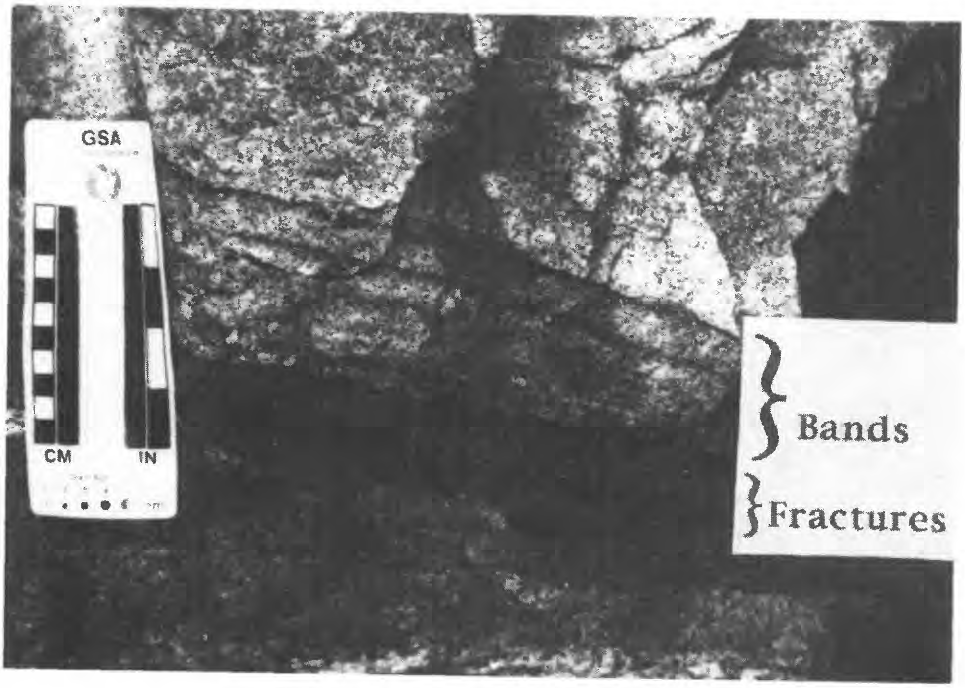

Figure 56. Liesegang bands in granite from Hubbard Brook watershed, New Hampshire.

bands form in times of tens to hundreds of years. Thus, Liesegang bands are "finger prints" of previous hydrologic conditions and suggest that diffusion has occurred in granite rocks in time scales that are important in consideration of toxic or radioactive-waste disposal or remediation.

Laboratory evaluation of diffusion in granites, schists, and basalt suggests that the effective diffusion coefficient (including porosity, sorption, and tortuosity) for ^{137}Cs is approximately 6.5 x 10^{-13} m^2/s. This value is similar to 1 x 10^{-13} m^2/s (meters squared per second) determined in a Swedish gneiss by Skagius and Neretnicks (1988). It can be seen from figure 57 that the ^{137}Cs ions have penetrated approximately 7 mm into granite over a period of 101 days. Effective porosity of 32 granite samples ranged from 1.07 to 2.33 percent with an average 1.46 percent.

Large scale diffusion (>10 m, thousands of years)

This scale of diffusion is represented by geologic time and is illustrated by diffusion from a saline lake through a 30-m-thick, low-permeability shale to an underlying freshwater aquifer. Diffusion at this scale is an important consideration for long-term storage of toxic or radioactive waste; that is, this site can be viewed as a natural surrogate for waste disposal in shale. The site is located on the Southern High Plains, 50 km south of Lubbock, Texas.

Figure 58 illustrates the relation between advection and diffusion in this one-dimension flow system. The vertical axis represents the relative thickness of the shale member; the horizontal axis represents the relative concentration. If only advection were present, concentration would be the same throughout the vertical profile. If diffusion

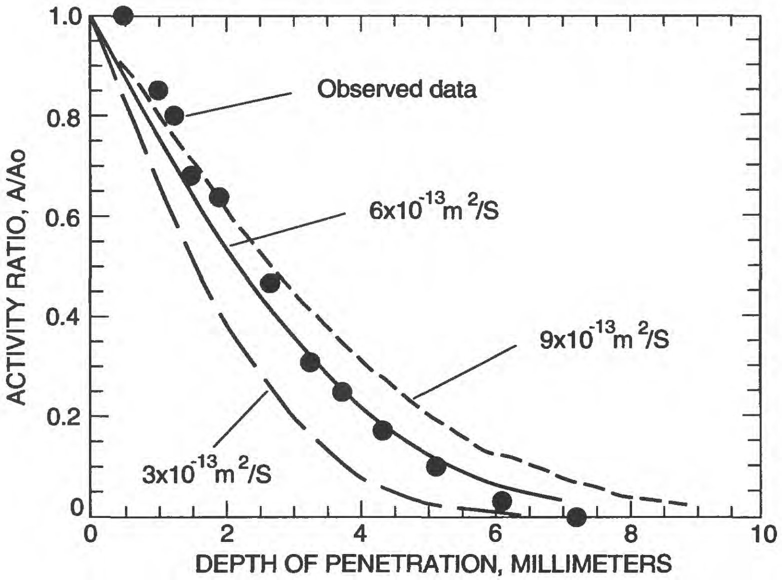

Figure 57. Relative activity and penetration distance of ^{137}Cs into granite from Mirror Lake, Grafton County, New Hampshire. Best fit yields an effective diffusion coefficient for ^{137}Cs of approximately 6×10^{-13} meters squared per second.

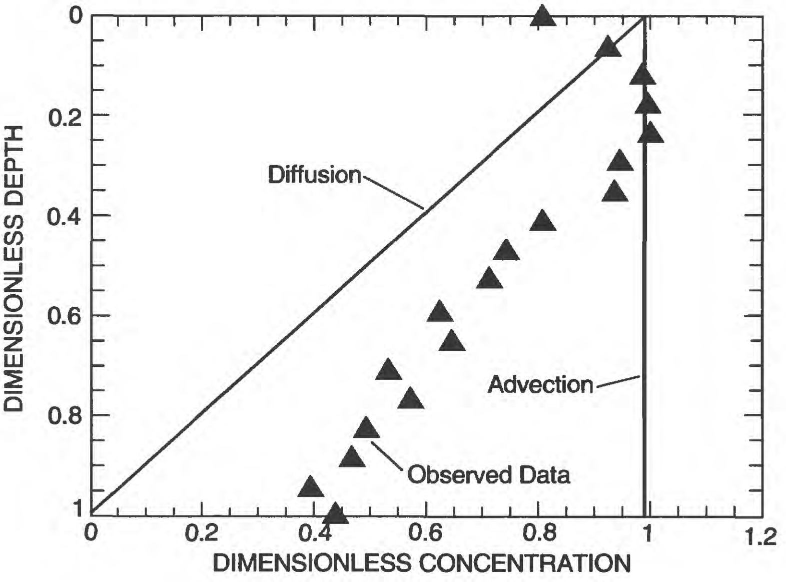

Figure 58. Observed chloride data from Double Lakes, Texas, relative to theoretical advection and diffusion models.

were the only transport mechanism, concentration would be represented by a straight line connecting the two concentrations. Any combination of diffusion and advection will generate a curved line.

Figure 58 illustrates an observed chloride profile through the shale collected with a dedicated multiple-level-sampling device that samples water at 1.5-m vertical intervals. A plot of the relative concentration as a function of relative distance suggests that solute transport through the shale occurs largely by diffusion. The upper two or three points are interpreted as a recent (last 5,000 yr) change in solute concentration in the lake that has not equilibrated and, thus, deviates from the theoretical diffusion curve. Hydrologic analyses suggests that traveltime through the 30 m of shale is approximately 30,000 yr (Ward Sanford, U.S. Geological Survey, oral commun., 1993).

Summary

The small, intermediate and large scales of diffusion illustrate its importance when considering geologic disposal of toxic or radioactive waste. The small (millimeter) scale is important in short-term tracer test experiments. The intermediate (10 mm-10 cm) scale is important in the time scale of months to tens of years, and can significantly change solute transport along fractures. Finally, large scale diffusion can transport a significant amount of mass on a geologic time scale with diffusion distances over tens of meters.

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USE OF BOREHOLE-RADAR METHODS TO DETECT FRACTURES IN CRYSTALLINE ROCKS, MIRROR LAKE AREA, GRAFTON COUNTY, NEW HAMPSHIRE

By F.P. Haeni *and* John W. Lane, Jr.

Introduction

Characterization of direction, number, and hydraulic properties of fractures and the resulting ground-water flow is an important component of ground-water contamination studies. The USGS established a fractured rock research site in the Mirror Lake area, Grafton County, New Hampshire (fig.59), for the purpose of conducting multidisciplinary research on the flow of contaminants in fractured bedrock. As one part of this research, borehole-radar surveys were conducted to

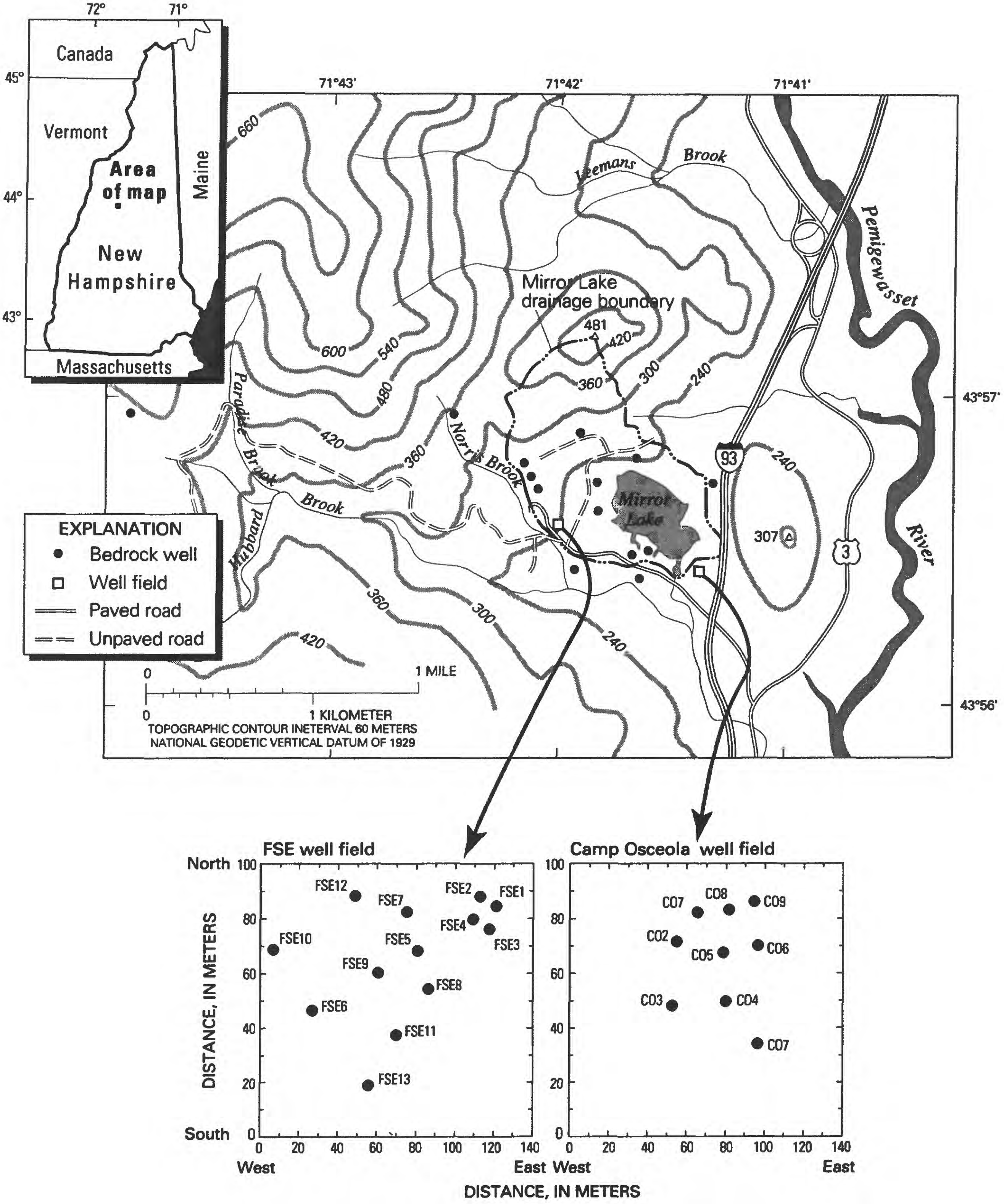


Figure 59. Location of U.S. Geological Survey fractured rock research site and borehole-radar survey sites, Mirror Lake area, Grafton County, New Hampshire.

detect bedrock fractures. This paper presents the results of borehole-radar surveys conducted at the Mirror Lake area, Grafton County, New Hampshire, in June 1991. Surveys were conducted at two sites—the Camp Osceola well field and the FSE well field (fig. 59). At these sites, crystalline bedrock, consisting of foliated schists intruded by granite, pegmatite, and basalt (C.C. Barton, U.S. Geological Survey, written commun., 1993), underlies 3 to 10 m of glacial drift.

Borehole-radar Equipment And Field Methods

Borehole-radar methods are similar to surface-radar methods, except that the transmitter and receiver are oriented vertically in a borehole. The transmitter and receiver are separated by a fixed distance when used in a single-hole configuration and can operate in a directional or nondirectional mode. Reflectors from subhorizontal saturated fractures are caused by the same physical property changes that cause surface-radar reflections and are usually coherent events. Borehole-radar methods were developed primarily to detect fractures at proposed high-level nuclear waste sites and have been used by Olsson and others (1988, 1992a, b) to detect fractures in crystalline rocks in Sweden. The application of this geophysical method to shallow ground-water contamination sites is new, and only a few demonstration projects have been conducted (Borje Niva, ABEM Inc, written commun., 1991).

The borehole radar unit used in this study, manufactured by ABEM Inc., has a nondirectional antenna with a center frequency of 22 and 60 Mhz and a directional antenna (consisting of four orthogonal antennas along a common axis) with a center frequency of 60 Mhz. For the single-hole surveys, the transmitter and receiving antenna centerpoints were separated by 8.1 to 14.2 m and were lowered down the hole by a computer-controlled winch. Readings were taken every 0.25 m, and 128 scans were stacked at each interval. All data were displayed in the field on a portable computer and were digitally recorded for further processing. Cross-hole tomography measurements were conducted by placing the receiver and transmitter in separate boreholes. The transmitter location was fixed, and the receiver location was moved in 3-m increments down the length of the second borehole. The transmitter was then moved 3 m and the process was repeated until the transmitter reached the bottom of the first borehole.

Processing and interpretation of the single-hole data included filtering and migration. This was performed using the RADAN processing package developed by GSSI and the RAMAC package developed by ABEM. Processing the cross-hole tomography data, using the conjugated gradient method, was performed with the RAMAC package.

Fracture Detection In The Mirror Lake Area

Single-hole borehole radar surveys were conducted in boreholes CO-1, CO-2, and FSE-5. Individual reflectors up to 60 and 80 m away from CO-1 and CO-2 were detected using the 60- and 22-MHz nondirectional antennas respectively (fig. 60). Directional data, using 60-MHz antennas, detected reflectors that were up to 30 m away from the borehole. Twelve reflectors, interpreted as fractures, were identified in CO-1, eight were identified in CO-2, and nine were identified in FSE-5. Data obtained with the directional antenna also allowed estimation of the azimuth, dip angle, and borehole-intersection depth of the reflectors; this information is presented in table 13. Fractures could be corre-

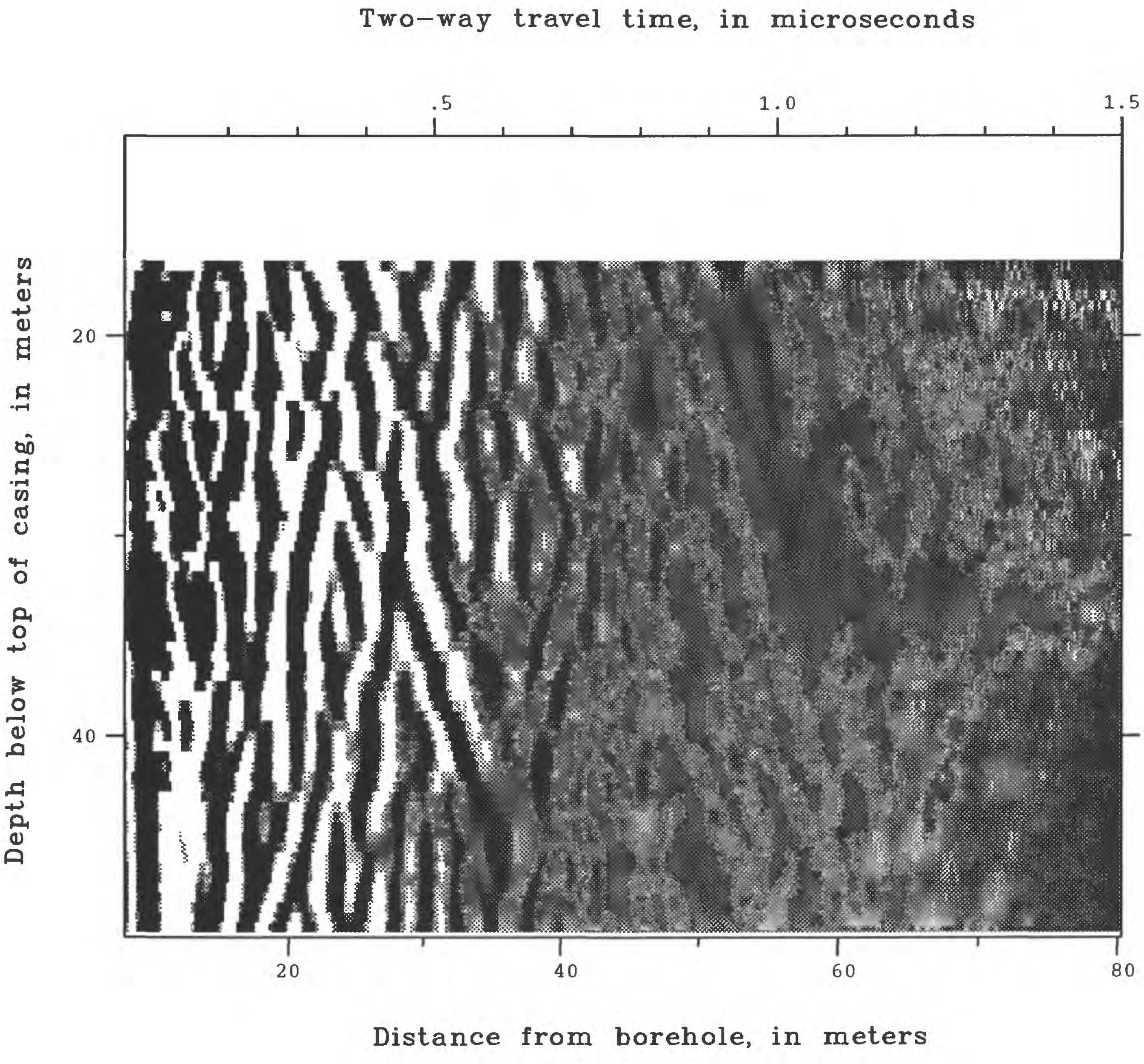


Figure 60. Borehole radargram, using 22-MHz nondirectional antenna, showing extent of reflectors (80 meters) from borehole CO-2.

Table 13. Azimuth, dip angle, and depth to intersection with borehole of identified reflector
[---, not applicable]

Borehole-intersection			Borehole-intersection			Borehole-intersection		
Azimuth	Dip angle (degrees)	Depth (meters)	Azimuth	Dip angle (degrees)	Depth (meters)	Azimuth	Dip angle (degrees)	Depth (meters)
Borehole CO-1			Borehole CO-2			Borehole FSE-5		
160	28.7	2.4	040	41.0	7.3	70	61	13.1
100	27.1	9.7	080	34.5	26	140	45	19.6
110	45	19	080	48.2	34.5	150	33.1	28.2
110	39	22.5	010	15.3	56.2	320	58.8	33.8
190	37.9	30	140	19.3	60	40	49.8	46.1
110	41.3	37.5	080	17.5	72.1	260	46.2	57.5
220	32	42.5	190	17.5	84	110	47.6	61.5
270	34.9	45.7	100	18.0	98	110	51.1	66.1
190	32.2	57.5				320	19.3	108.5
180	25.2	76.5						
210	30	83.5						
---	90	56						

lated between CO-1 and CO-2 (located 20 m apart) in some, but not all, cases. Some reasons for this could be that fractures are not generally planar, fractures may be discontinuous over the interval between the two boreholes, or fracture reflectors may be masked by other fractures.

Fractures located between the transmitter and receiver can cause scattering and attenuation of the radar pulse—the amplitude of the direct arrival of the radar pulse decreases as the number of fractures and the hydraulic conductivity increases. Therefore, a plot of the amplitude of the direct arrival of the radar pulse from the transmitter to the receiver against the measurement location (fig. 61) can be interpreted as qualitative indicator of the number of fractures located between the transmitter and the receiver.

Physical properties affecting radar-wave propagation are different for rocks and water--radar velocity is much lower and the pulse attenuation is generally much higher in water than in rock. Cross-hole radar tomography between boreholes FSE-1 and FSE-4 (located 15 m apart) showed a low-velocity/high-attenuation zone at a depth of 35 to 50 m (fig. 62). Assuming the rock properties are uniform between the boreholes, this low-velocity/high-attenuation zone can be interpreted as a zone of saturated fractures. This interpretation agrees with other geophysical and hydrologic

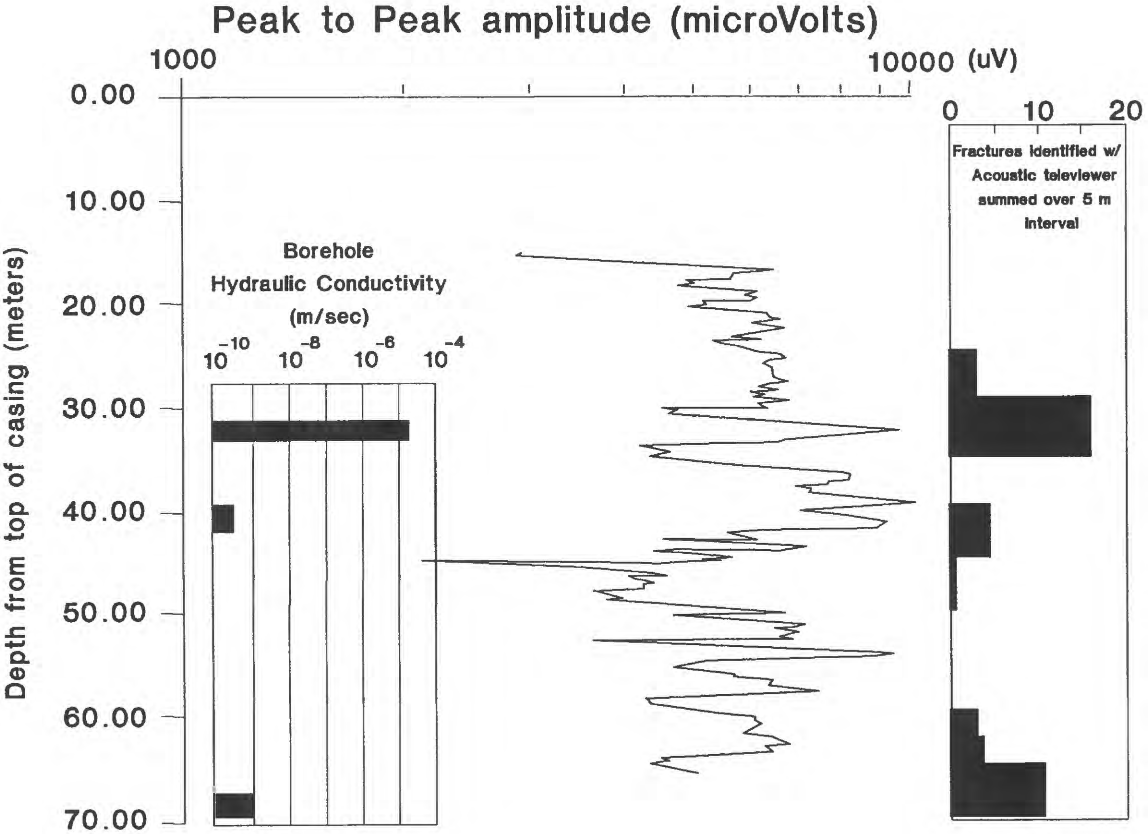
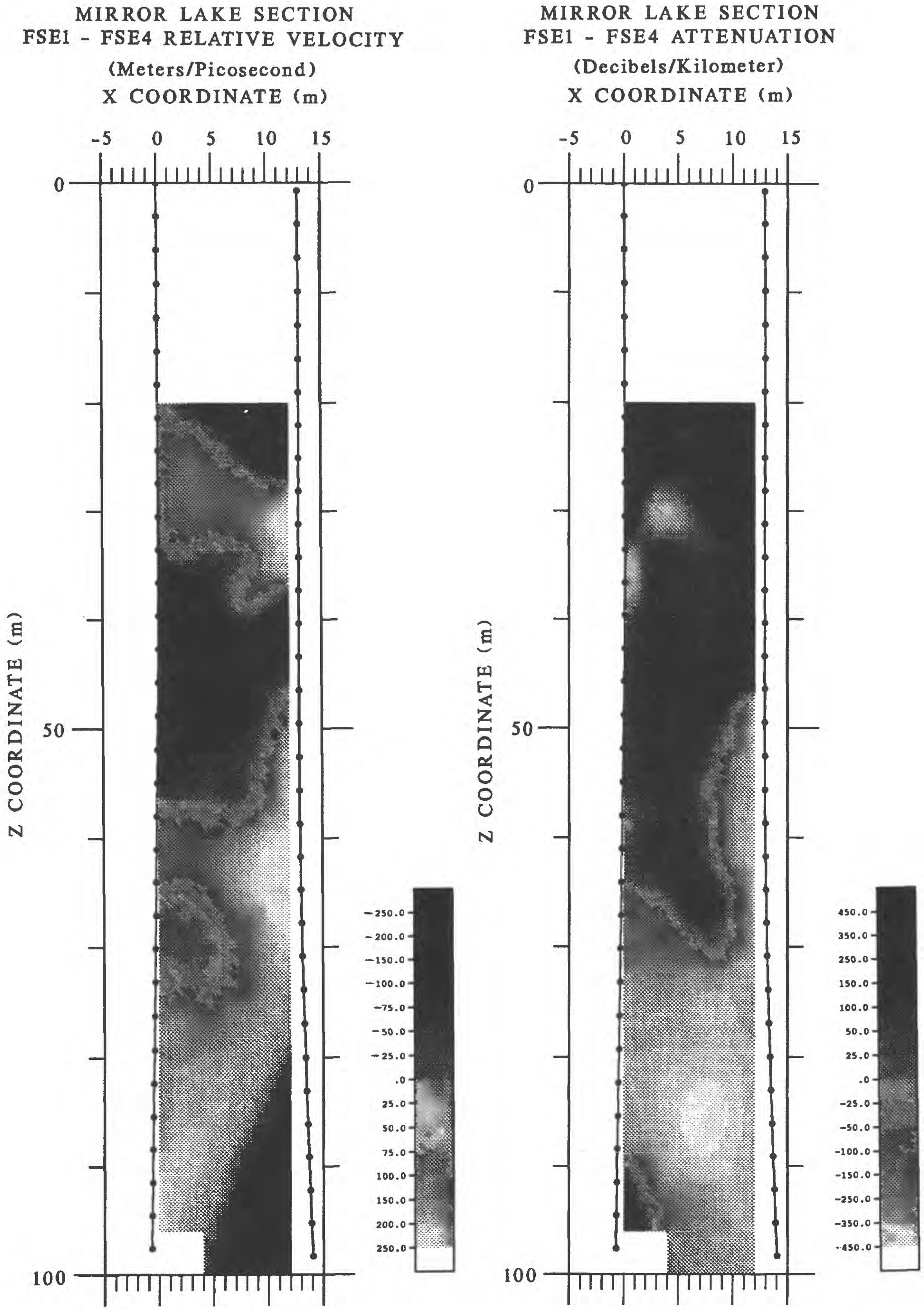


Figure 61. Amplitude of the direct arrival of the radar pulse between the transmitter and receiver plotted against measurement location.

data from these two boreholes, including seismic tomography, aquifer tests, tracer tests, and other borehole data.

Summary

Single-hole directional and nondirectional borehole-radar surveys were conducted in CO-1 and CO-2 at the Camp Osceola well field and in FSE-5 at the FSE well field. Individual fractures or fracture zones were identified up to 80 m away from the boreholes using the nondirectional antennas and up to 30 m away using the directional antenna. Cross-hole radar tomography, conducted between FSE-1 and FSE-4 at the FSE well field showed a low-velocity/high-attenuation zone between 35 and 50 m deep. This zone was interpreted to be a saturated fracture zone; this interpretation agrees with other geophysical and hydrologic data collected from the two holes.



MIRROR LAKE SECTION
FSE1 - FSE4 RELATIVE VELOCITY
(Meters/Picosecond)

MIRROR LAKE SECTION
FSE1 - FSE4 ATTENUATION
(Decibels/Kilometer)

Figure 62. Slowness and attenuation tomograms from boreholes FSE-1 and FSE-4.

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AN OVERVIEW OF FIELD INVESTIGATIONS OF FLUID FLOW IN FRACTURED CRYSTALLINE ROCKS ON THE SCALE OF HUNDREDS OF METERS

By Paul A. Hsieh

Introduction

A major question confronting researchers on fluid flow in fractured rocks is how to deal with the highly heterogeneous distribution of hydraulic properties in a rock mass. In crystalline rocks, for example, the hydraulic conductivity can vary by several orders of magnitude over a distance of several meters. Theoretical treatment of such heterogeneities includes representing the rock as an equivalent continuum, using stochastic processes to represent the heterogeneity in a probabilistic manner, and explicitly modeling the heterogeneities through detailed characterization. While it is not clear that any single approach is preferred, field investigations at a number of crystalline-rock research sites are beginning to provide guidelines on the usefulness of the different approaches. This paper provides a brief survey of the findings from these research sites, and presents some preliminary results from an ongoing study in the Mirror Lake area, New Hampshire, where the USGS is conducting research on fluid flow and chemical transport in fractured rocks. In each instance, subsurface characterization on the scale of hundreds of meters revealed the presence of highly permeable fracture zones or clusters of connected fractures. Explicitly identifying and characterizing these highly permeable zones were crucial to understanding flow in the rock mass.

Survey of Findings From Crystalline-Rock Research Sites

Construction of the Underground Research Laboratory in southeastern Manitoba represents a major Canadian effort to investigate the suitability of crystalline rocks for storage of nuclear waste. The laboratory consists of a 450-m-deep vertical shaft with horizontal tunnels at different levels. Prior to shaft excavation, a site investigation found three major low-angle fracture zones and a number of subvertical fracture zones. Based on this information, a model was developed to predict the inflow into the shaft during excavation, and the drawdown at packer-isolated intervals in a network of monitoring wells. The predicted drawdowns were relatively close to the actual drawdowns, but the predicted inflow was approximately four times the actual inflow. Nevertheless, according to Davidson (1986), the most important information for model development was the identification of the fracture zones.

At the Chalk River Laboratories in Ontario, Canada, characterization of a 200 m by 150 m by 50 m block of monzonitic gneiss revealed the presence of four extensive fracture zones: two are horizontal, one is inclined, and one is vertical. The rock mass surrounding the fracture zones is also fractured and permeable, although not as highly permeable as the fracture zones. To analyze a multiple-borehole hydraulic test at this site, Carrera and Heredia (1988) used a finite-element model in which the fracture zones were explicitly modeled as two-dimensional planar features while the rock mass was represented as a continuum. To limit the number of model parameters, homogeneity was assumed within each fracture zone and within the rock mass. Using this approach, Carrera and Heredia were able to calibrate the model so that the computed drawdowns closely match the observed drawdown. The results suggest that the fracture zones must be explicitly identified and included in the model in order to understand flow in the rock block.

In central Sweden, the Finnsjon site serves as a research facility for studying fluid flow in crystalline rocks. Of the many fracture zones encountered at the site, the low angle "Zone 2" has been most extensively studied through boreholes drilled in a 500 m by 500 m area (Ahlbom and Smellie, 1991). This fracture zone is approximately 100 m thick and lies at a depth between 100 m to 400 m below land surface. Near the top of Zone 2, a narrow subzone has significantly higher transmissivity. Hydraulic tests in this subzone show fast response over a distance of 400 m. Under natural hydraulic gradient, a tracer travelled this distance in one month. These findings suggest that Zone 2 is a major conduit that exerts a strong control on groundwater flow at the Finnsjon site.

Perhaps the best known site for crystalline rock research is the Stripa site in Sweden. As a part of the Site Characterization and Validation Project, the adequacy of characterization was tested by predicting the inflow into a cluster of six, 100-m-long, parallel boreholes, known as the "D boreholes" (Black and others, 1990). Based on hydraulic and fracture data from nearby boreholes, it was expected that the D boreholes would intersect several highly-permeable fracture zones within the fractured rock mass. Using identical field data but different modeling approaches, three independent groups of hydrologists made inflow predictions. In terms of total inflow, all three predictions were within a factor of two of the measured total inflow. However, the predicted distribution of inflow along the boreholes did not agree well with the measured distribution. Of particular interest is the fact that a majority of the prediction effort centered on calculating inflow from the fractured rock mass, while the majority of the actual inflow (approximately 90 percent) entered the boreholes via the fractured zones. Thus, the exercise demonstrates the importance of fracture zones in controlling flow through fractured rocks.

USGS Research on Fractured Rock Hydrology in the Mirror Lake Area

Similar to findings at the research sites surveyed above, results from the Mirror Lake area in central New Hampshire (fig. 59) underscore the importance of identifying the connected network of highly-permeable fractures within a less-permeable fractured rock mass. The Mirror Lake area is the site of an ongoing research effort by the USGS to study fluid flow and chemical transport in fractured rocks. As discussed by Shapiro and Hsieh (1991), the objectives of the study are to develop monitoring and testing methods for characterizing flow and transport in bedrock, and to establish a site for long-term study. Although the Mirror Lake area is not contaminated, the techniques and understanding developed in this study are directly transferable to other fractured rock sites that have been contaminated with hazardous wastes.

Among the many studies in the Mirror Lake area, a detailed investigation focuses on a 120 m by 80 m area known as the FSE well field. Here, approximately 20 m of glacial drift overlies the bedrock, which consists of schist that is intruded by granite and pegmatite. Thirteen wells have been drilled to depths ranging from 61 m to 229 m. Downhole acoustic televiewer and video camera logs show that each well intersects tens of fractures over the upper 50 m of bedrock, where active ground-water circulation occurs. However, hydraulic tests show that only a few of these fractures conduct significant amounts of flow. Furthermore, these highly permeable fractures connect with each other locally to form highly permeable zones within the less permeable fractured rock. Based on multiple-well hydraulic tests, four such highly permeable zones have been identified at the FSE well field (fig. 63). In such a setting, the response to a multiple-well hydraulic test is entirely different than the response in a homogeneous aquifer. If two packer-isolated intervals straddle the same highly permeable zone, the drawdowns in the intervals tend to be identical. In contrast, if

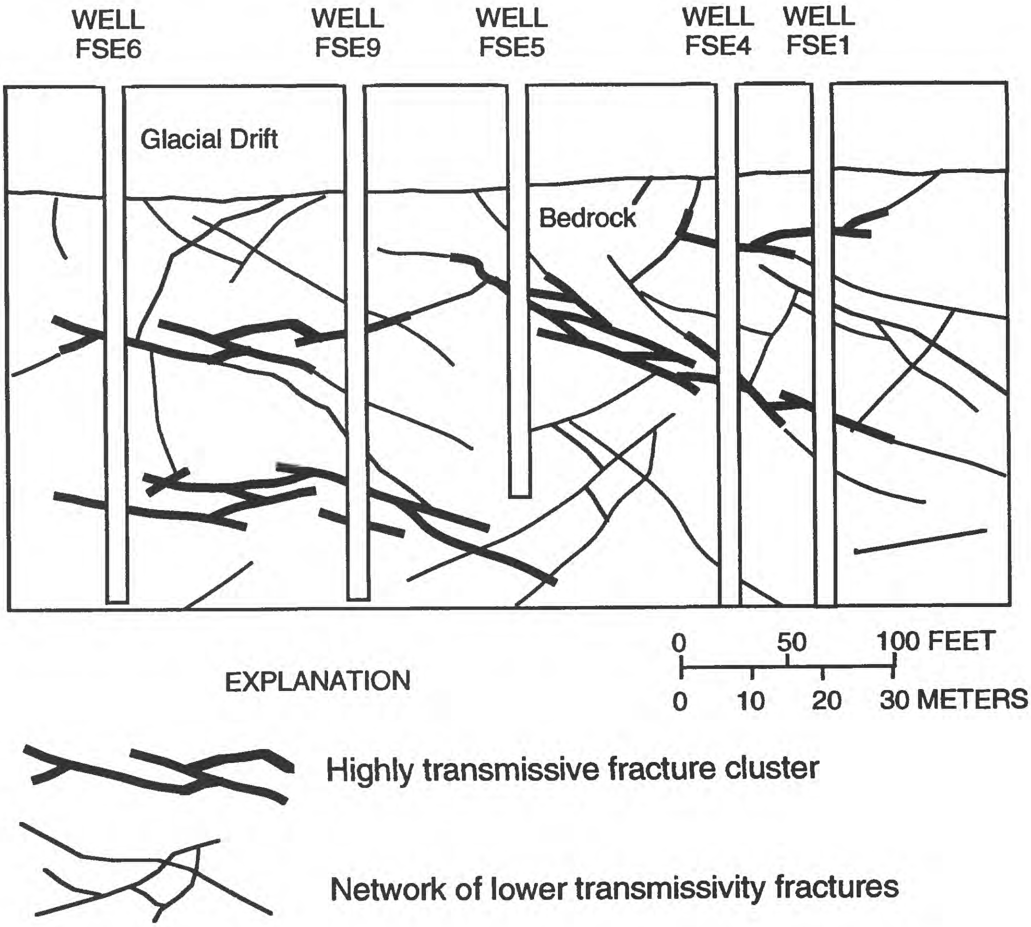

Figure 63. Vertical cross section between wells FSE-1 and FSE-6 at the FSE well field. Four clusters of highly permeable fractures occur within the less permeable fractured rocks.

two packer-isolated intervals straddle different highly permeable zones, the drawdowns are significantly different. Without explicitly recognizing the influence of the highly permeable zones, it would be virtually impossible to interpret the hydraulic tests.

Conclusions

A brief survey of findings from crystalline rock research sites shows that, in each case, subsurface characterization on the scale of hundreds of meters revealed the presence of highly permeable fracture zones or clusters of connected fractures. Explicitly identifying and characterizing these highly permeable zones was crucial to understanding flow in the rock mass. Similar results were also obtained at the Mirror Lake area in central New Hampshire, where the USGS is conducting research on fluid flow and chemical transport in fractured rocks.

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ESTIMATION OF EFFECTIVE POROSITY IN FRACTURED CRYSTALLINE ROCK BY CONTROLLED-TRACER TESTS

By Allen M. Shapiro

Introduction

The characterization of geologic environments, such as crystalline rock, for high- and low-level radioactive-waste isolation requires a detailed hydrogeologic investigation in the immediate vicinity of the repository site—for example, over distances of tens of meters. The characterization of chemical transport over these distances requires the identification of physical properties of the formation, such as the effective porosity. The effective porosity relates the mean volumetric flow rate (as defined by the Darcy flux) to the mean fluid velocity; it is the mean fluid velocity that controls the mean displacement of chemical constituents. Laboratory estimates of porosity can be made only for the unfractured rock matrix. The effective porosity of fractures, which are the principal conduits of ground-water flow and chemical transport, cannot be identified from the laboratory analyses of cores. The area of a fracture intersected by a core is not representative of the entire fracture or of many interconnected fractures. Consequently, the effective porosity of fractured rock must be inferred from controlled chemical-transport experiments conducted under field conditions at the scale of the investigation.

Controlled-tracer experiments involve the introduction of a dissolved chemical constituent, referred to as a tracer, into the subsurface and the monitoring of either the spatial distribution of the tracer concentration at several times or the temporal variation of the tracer concentration at one or more fixed locations. With a knowledge of the (hydraulically stressed or ambient) flow regime, the effective porosity can be estimated. Controlled-tracer experiments usually are viable over distances of tens of meters; over larger distances and longer times, it becomes more difficult to account for the entire mass of the tracer that has been introduced into the flow regime. However, controlled-tracer experiments in fractured crystalline rock are most likely to be successful in estimating effective porosity if they are performed under hydraulically stressed conditions that ensure that the tracer will be recovered at specific sampling locations—for example, where fluid is extracted from the formation (Shapiro and Nicholas, 1989).

This article discusses the estimation of effective porosity in two tracer tests conducted under hydraulically stressed conditions in the crystalline bedrock of the Mirror Lake watershed located in the Hubbard Brook Experimental Forest in Grafton County, New Hampshire (fig. 59). The Mirror Lake watershed is the site of a USGS investigation into the development and evaluation of field techniques and interpretive methods of characterizing ground-water flow and chemical transport in fractured rock over distances ranging from meters to kilometers (Shapiro and Hsieh, 1991). The bedrock in the Mirror Lake watershed is primarily a sillimanite-grade schist that has been extensively intruded by granite and pegmatite and by lesser amounts of basalt.

Description And Results Of Tracer Tests

The tracer tests discussed in this article were conducted in a cluster of bedrock wells, referred to as the FSE well field (fig. 59). In the FSE well field, several subhorizontal permeable features of limited areal extent were identified using a combination of borehole geophysics, single-hole fluid injection tests in bedrock wells, and (hydraulic) interference tests where an hydraulically isolated section of a bedrock well was pumped and the fluid pressure was monitored in hydraulically isolated sections of the other bedrock wells. The subhorizontal permeable features in the FSE well field do not represent individual subhorizontal fractures. Instead, they are the result of the interconnection of many permeable fractures that are of different orientations. In addition, there are many other fractures throughout the rock exhibiting a wide range of hydraulic conductivities and orientations.

The tracer tests that are discussed in this article were conducted in one of the subhorizontal permeable features that intersects bedrock wells FSE-6, FSE-9, FSE-11 and FSE-13 (fig. 59). Tracer tests were conducted by isolating the permeable feature in these bedrock wells using inflatable packers. Inflatable packers were also installed in all other bedrock wells in the FSE well field to eliminate the influence of the vertical permeability associated with open boreholes. In the tracer tests discussed in this article, the isolated interval in FSE-6 (29.2 m to 37.9 m below top of casing) was pumped continuously at a rate of 1.67×10^{-3} m^3/s. The initial transient response associated with pumping was allowed to equilibrate over 24 hours, and a tracer test was started on August 6, 1992, by injecting a sodium-bromide solution in the hydraulically isolated interval of FSE-9 (42.6 m to 43.3 m below top of casing). A second tracer test was started on August 8, 1992, with the injection of a sodium-bromide solution into the hydraulically isolated interval in FSE-11 (45.7 m to 46.4 m below top of casing). The bromide concentration was monitored from samples collected at the pumped well. Boreholes FSE-6 and FSE-9 are separated by 36.3 m and boreholes FSE-6 and FSE-1 are separated by 43.7 m.

The bromide concentration at the pumped well for the two tracer tests is shown in figure 64, where bromide concentrations have been adjusted to account for the background concentration and the overlap of the two tests. The bromide concentration at the pumped well associated with the tracer injection into FSE-9 (fig. 64*A*) shows an extremely steep rising limb and a rapid decline in comparison to the bromide concentration at the pumped well associated with the injection into FSE-11 (fig. 64*B*).

The percentage of the recovered mass from each of the tracer tests is also shown in figure 64. In the tracer test from FSE-9, over 80 percent of the injected mass was recovered. This calculation, however, is based on the average pumping rate. If fluctuations in the pumping rate are also considered, estimates for the percentage of the mass recovered increase to approximately 90 percent. The percentage of mass recovered in the tracer test from FSE-11 is over 80 percent at the time this test was terminated. Because of the gradual declining limb in the bromide concentration in this test, the percentage of the recovered mass was still increasing sharply when the test was terminated. In contrast, the percentage of the mass recovered from the tracer injection in FSE-9 appears to have approached an asymptotic limit.

The hydraulic response due to pumping FSE-6 resulted in an almost uniform drawdown in the permeable subhorizontal feature where the tracer tests were conducted (P.A. Hsieh, U.S. Geological Survey, written commun., 1992). In addition, drawdowns were measured in the permeable zones above and below the permeable feature where the tracer tests were conducted, indicating the principle source of water entering the zone being tested is vertical leakage through less permeable fractures.

The results of the hydraulic test indicate that the subhorizontal permeable feature behaves as a near-infinite permeability zone, however, the results of the tracer tests demonstrate the significant heterogeneity in this permeable feature. The results of the tracer tests indicate that bedrock well FSE-11 is probably located within a lower permeable area of the otherwise highly permeable zone. Furthermore, it is apparent that a radially uniform flow regime (with vertical leakage) has not been established due to pumping from FSE-6. Therefore, assumptions of an homogenous hydraulic conductivity field could lead to erroneous estimates of the effective porosity in the interpretation of the tracer tests. A heterogeneous hydraulic conductivity and effective porosity need to be considered in estimating the formation properties in order to reproduce both the hydraulic response due to pumping and the bromide concentration at the pumped well from each tracer test. In addition, other processes, such as diffusion of the

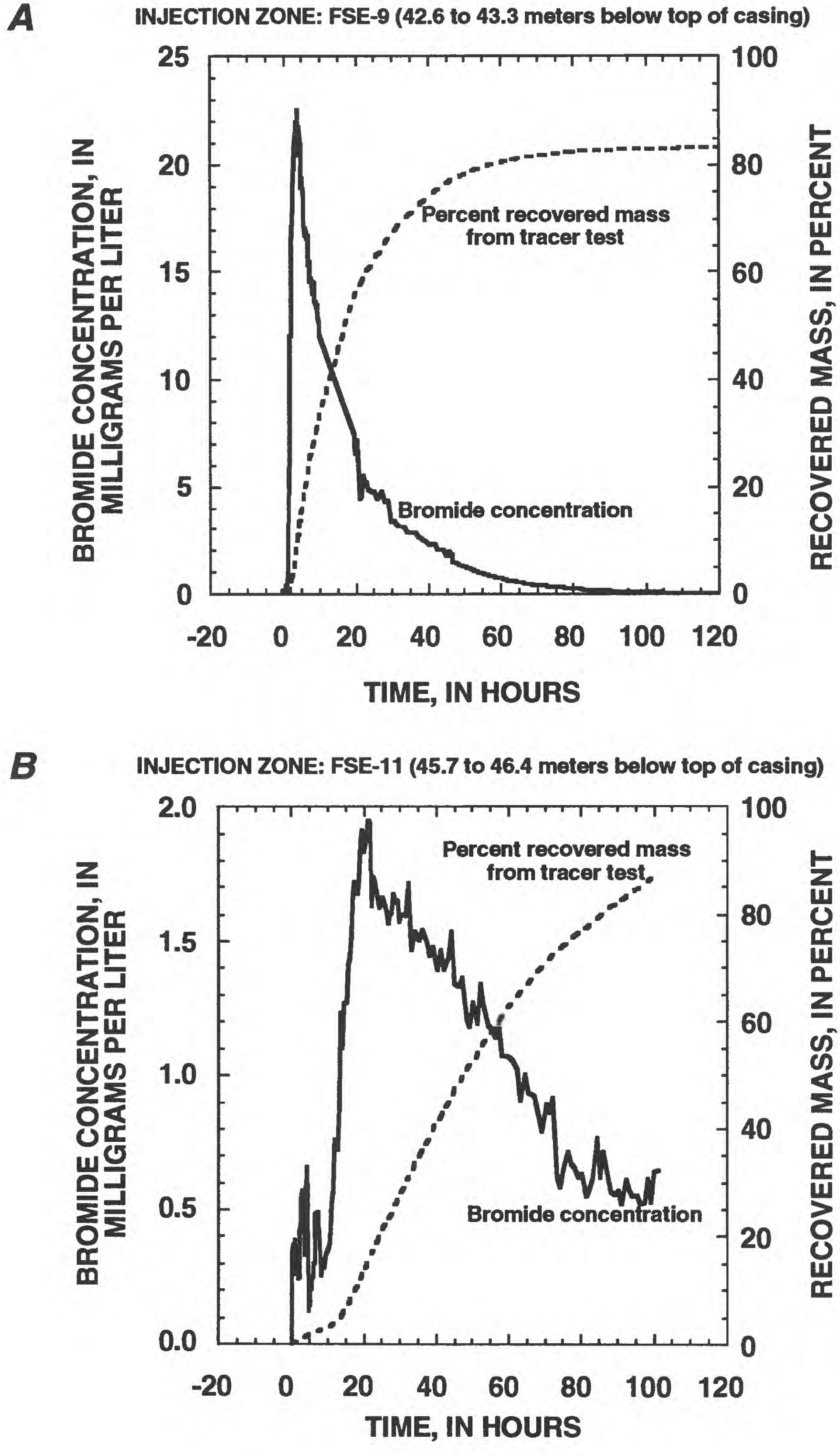

Figure 64. Bromide concentration as a function of time in bedrock well FSE-6 for tracer injection in (*A*) bedrock well FSE-9 and (*B*) bedrock well FSE-11.

tracer into the rock matrix may also play a role in characterization of effective porosity in fractures in crystalline rock.

Nevertheless, it is of interest to identify estimates of the effective porosity from each tracer test using the relationships for a homogenous flow regime in the absence of matrix diffusion. However, these results should only be regarded as estimates subject to more detailed modeling efforts that account for the heterogeneity in the flow regime and matrix diffusion. Assuming steady-state, radially converging fluid movement to the pumped well, the porosity is defined as

$$Bn = \frac{\bar{t}Q}{2\pi R^2 f(\alpha)} \qquad (28)$$

where B is the formation thickness, n is the porosity, $\bar{t}$ is the mean arrival time associated with the measured concentration at the pumped well, Q is the pumping rate, R is the distance between the pumped well and the injection well, and $f(\alpha)$ is a function of the vertical leakage, where $\alpha = R(K'/B'T)^{1/2}$, K' is the vertical hydraulic conductivity, B' is the thickness of the lower permeability zone above the tested interval and T is the transmissivity of the tested interval. Using the leaky-aquifer solution of Hantush and Jacobs (1955), and considering steady-state fluid movement, the function of $f(\alpha)$ is defined as

$$f(\alpha) = \int_{\frac{r_w}{R}}^{1} \frac{dr'}{K_1(\alpha r')} \qquad (29)$$

where K_1 is the modified Bessel function of the second kind of order one, and r_w is the radius of the pumped well.

From estimates of the leakage parameters obtained from the hydraulic tests (P.A. Hsieh, U.S. Geological Survey, oral commun., 1993), B' = 35 m, K' = 10^{-7} m/s and T = 5×10^{-5} m^2/s, the estimate of Bn obtained from the results of the tracer test conducted from FSE-9 is 10^{-4} m, while the estimate for Bn from the test conducted from FSE-11 is 10^{3} m. The difference between the estimates of Bn is due to the difference in the mean arrival time and the difference in distances between the pumped well and the injection well for each test.

The estimates of the porosity cannot be separated from the parameter B, which represents a uniform formation thickness. In conducting tracer tests in isolated permeable intervals in fractured rock, it is difficult to identify a meaningful formation thickness, because transport occurs through an interconnected network of fractures. For this reason, many investigations regard the product of B and n as an equivalent fracture aperture (Tsang, 1992). This estimate of fracture aperture, however, is based on the residence time of a tracer. A different effective aperture would result in the interpretation of the transmissivity obtained from hydraulic tests.

Summary and Conclusions

Fractures are the principle conduits of ground-water flow and chemical transport in crystalline rock. Estimates of the effective porosity of fractures must be made by conducting controlled-tracer tests under field conditions. Usually, assumptions, such as homogeneity and isotropy, are invoked in estimating the porosity of discrete highly permeable fractures or fracture zones in crystalline rock. To illustrate the complexity of estimating the effective porosity of fractures in crystalline rock, two tracer tests were conducted in a highly permeable fracture zone (intersected by several boreholes) in the crystalline rock of the Mirror Lake watershed in central New Hampshire. The tests were conducted by pumping one borehole continuously while injecting a slug of a sodium-bromide solution into an adjacent borehole. The two tests were conducted between sets of boreholes at different orientations and separated by approximately 36 and 44 m, respectively. Fluid pressure responses to pumping could not distinguish heterogeneity in the fracture zone. Plots of bromide concentration versus time at the pumped well for the two tests indicated the heterogeneity of the fracture zone.

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AN OVERVIEW OF THE UCLA-NRC LOW LEVEL WASTE PROGRAM—COVER PERFORMANCE, ANION RETENTION, TRITIUM MIGRATION MODEL

By Robert K. Schulz *and*
Edward O'Donnell

Introduction

Infiltration of water into waste is the foremost problem associated with near-surface disposal of Low Level Waste (LLW). Clearly, it is advantageous to reduce water infiltration to buried waste to as low a level as is reasonably achievable. This work examines and demonstrates various cover designs that can be used for achieving that goal (O'Donnell, Ridky, and Schulz, 1992). A brief summary of our activities on cover designs is given below under the heading "Cover Performance."

The long-lived radioisotopes of iodine and technetium may be present in waste as anions, and as such they will tend to move freely through soils by water transport. This work investigates the possibilities of finding and evaluating unusual volcanic soils that might have anion exchange properties which would be useful in retarding these anions (Gu and Schulz, 1991; Schulz, O'Donnell, and Duckart, 1992). If such soil material is found, it could be used to condition the near-field environment around waste. Our work is described below under the heading "Anion Retention."

There is concern about the possibility that tritium buried at the Nevada Test Site and proposed for burial at Ward Valley, California, may appear at the soil surface in the vapor phase, or will contaminate the ground water. This work analyses transfer of tritium from a point of release in a uniform, relatively dry soil. It also provides a basis for design of field experiments to better define the risks and opportunities associated with this form of waste management. The study is described below under the heading "Tritium Migration Model."

Cover Performance

By Robert K. Schulz, Edward O'Donnell, *and* R.W. Ridky

This study seeks to control water infiltration through waste disposal unit covers in humid regions. Experiments are being performed in large-scale lysimeters (75' × 45' 'x 10') at Beltsville, Maryland. The results are applicable to disposal of LLW, uranium mill tailings, hazardous waste, and sanitary landfills.

Three kinds of waste disposal unit covers or barriers to water infiltration are being investigated. They are: (1) resistive layer barrier (clay), (2) conductive layer barrier, and (3) bioengineering management. The conductive barrier consists of a conductive layer in conjunction with a capillary break. During unsaturated flow the conductive layer "wicks" water around the capillary break. This is demonstrated in the experiments carried out at Beltsville, Maryland (O'Donnell, Ridky, and Schulz, 1992). Below-grade layered covers (1) and (2) will fail if there is appreciable subsidence of the cover. Remedial action will then be difficult. Bioengineering management overcomes this problem because it is easily repairable if damaged by subsidence; therefore, it could be the system of choice under active subsidence conditions. "Bioengineering management" uses a combination of engineered run-off and stressed vegetation in an overdraft condition to control water percolation through disposal unit covers. Vegetation planted (in this case, junipers) between areas of impermeable cover extend over the cover to intercept incoming solar energy to evaporate water. Roots extend under the cover in all directions to obtain water. The performance of two plots (or lysimeters) are given in figure 65. Initially the water tables were at 1 and 2 m.. In about 2 yr, the plots

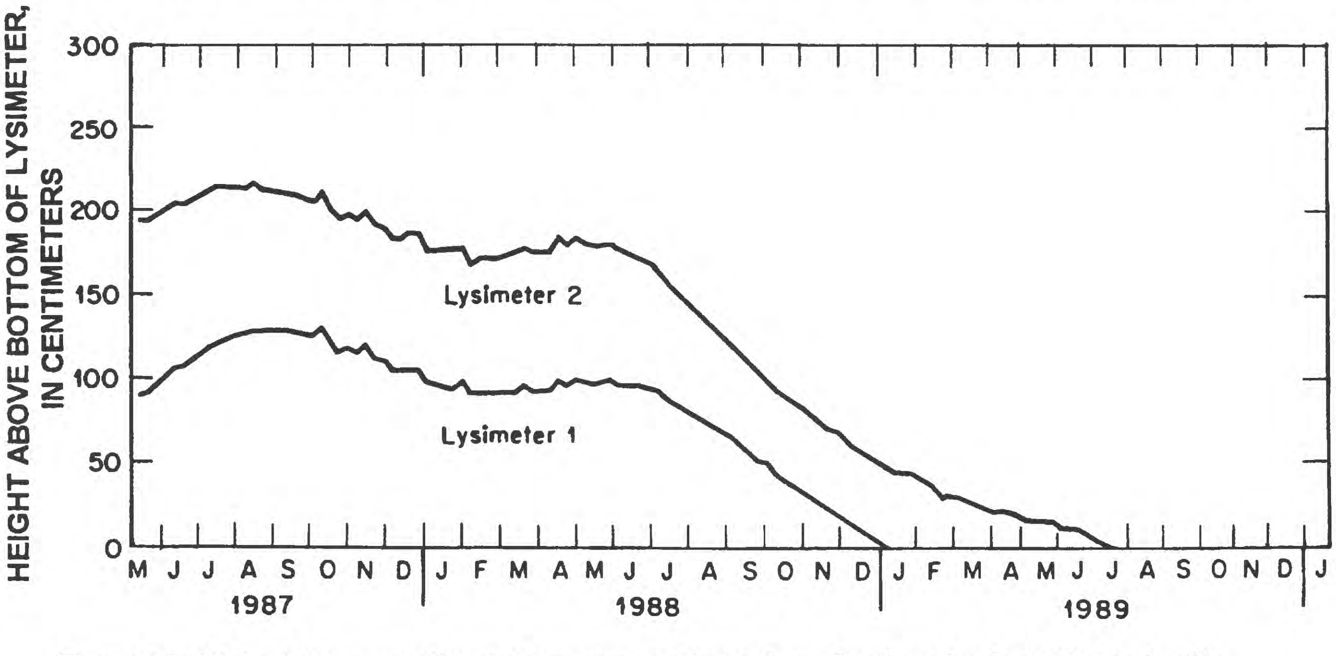

Figure 65. Water table versus time in bioengineered lysimeters. Decline of water table levels with passage of time shows bioengineered covers were very effective in preventing water percolation. Elimination of water table shows that this procedure could be used for remedial action ("drying out") of existing water-logged burial sites.

were completely dewatered. Subsequently, the system was maintained in a very dry state as shown in figure 66. Compare this result with the performance of reference lysimeters 3 and 4 (fig. 67) where the plots were cropped to fescue grass and the water table reached the surface in one year. After using this system for an extended period of time and subsidence ceases, the bioengineering system could be replaced by a resistive layer barrier/conductive layer barrier system. No further significant maintenance would then be required. If a clay barrier alone is used to control water infiltration to the waste, the cover will be "sensitive," that is, sensitive to imperfect construction or degradation by penetrating roots. The roots will die and decay, causing markedly increased permeability of the clay with the passage of time. A system using a conductive layer under the clay layer as a water scavenging system will, in comparison, be "robust." Roots will still degrade the clay layer, but will not degrade the scavenging layer. A root hole through the conductive layer will be analogous to a hole through a wick. It will do no significant damage. The

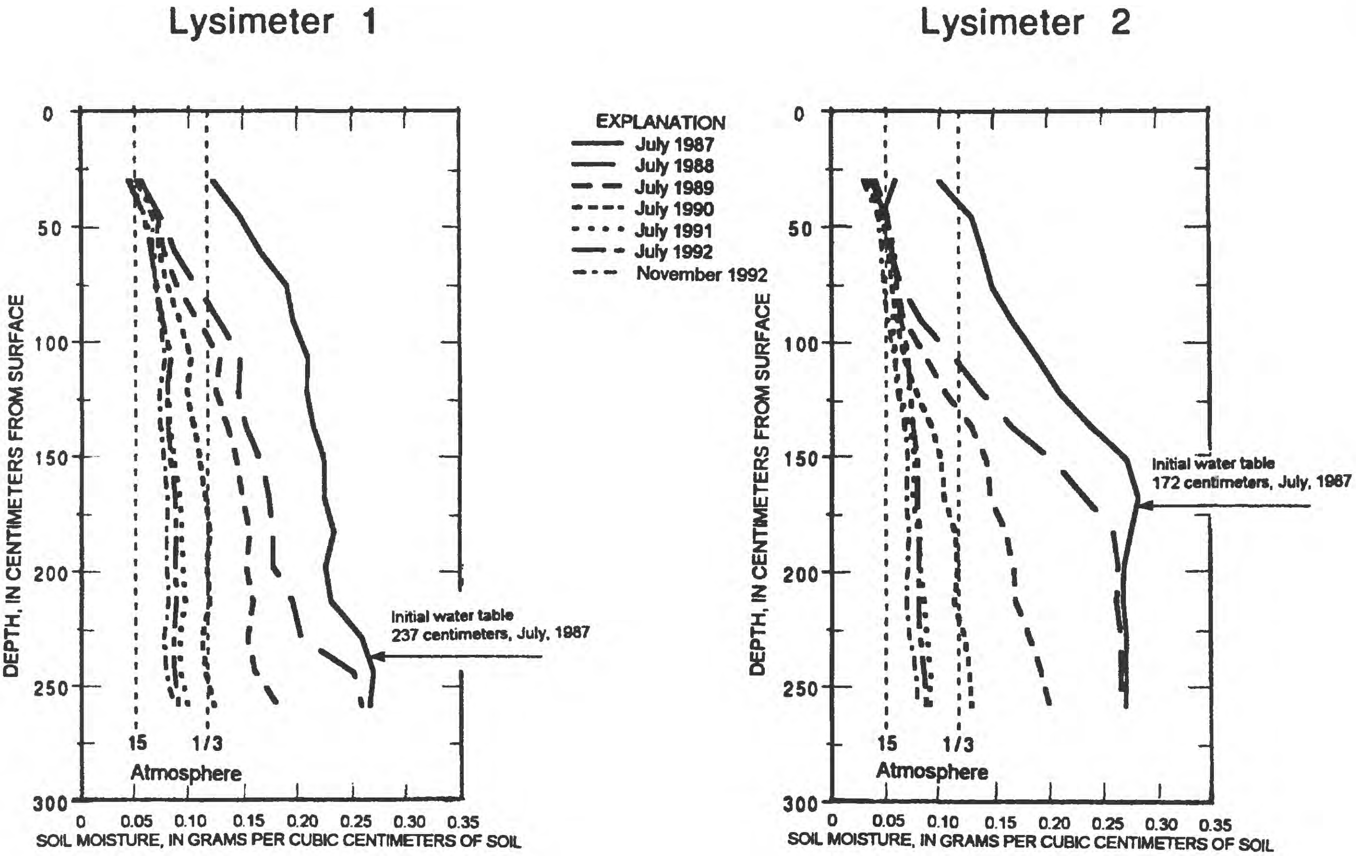

Figure 66. Bioengineered covers. Volumetric soil moisture content plotted as a function of soil depth seven different dates. By July of 1989, water table had been eliminated from soil profiles. As of November 1992, entire soil profiles, although relatively dry, still showed slightly increasing moisture content with depth.

combination of a resistive layer with a conductive (scavenging) layer underneath is thus less dependent on perfect construction techniques, and will be resistant to damage by root invasion. In the absence of subsidence such a system will function effectively for millennia.

Another very useful application of the resistive layer barrier/conductive layer barrier system would be in the protection of an earth mounded concrete bunker disposal unit. In that case, the barrier system would shield the concrete from exposure to flowing water. The resulting stagnant alkaline film of water would tend to protect the concrete from degradation over a long time period. Similarly, a resistive layer barrier/conductive layer barrier system could be used to protect high level waste. If high level waste was disposed of in a rock formation with a fracture present, this system could be used to divert possible fracture flow water around the waste.

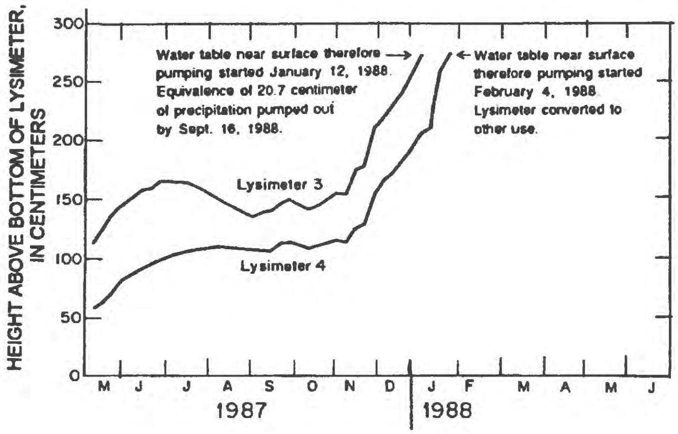

Figure 67. Water table versus time in reference lysimeters. The crowned surface is cropped with fescue grass. Water table increased with time until pumping of water table was necessary to keep trench from running over. Surface run-off was 8 percent of precipitation.

Anion Retention

By Robert K. Schulz, E.C. Duckart, *and* Edward O'Donnell

Because of their cation exchange capacity, most soils are effective in retarding cation migration. Performance of radioactive waste disposal facilities could be improved by conditioning the near-field environment either in or around radioactive waste disposal units with agents that will bind up long-lived radionuclides such as ^{129}I and ^{99}Tc that might migrate in the anionic form as iodide, iodate, and pertechnate.

Literature review (Gu and Schulz, 1991) and thermodynamic considerations indicate that because of their anion exchange capacity (AEC), soils containing the amorphous clays allophane and imogolite, have the potential to greatly reduce the migration of anions.

To follow up on the literature review, we are prospecting in areas with volcanic parent material to determine if significantly large deposits of soils with high anion exchange capacity are available. Sampling and laboratory testing are underway. Preliminary results are promising and they show significantly greater iodine adsorption on soils developed from ash rather than those developed from lava. To date, we have investigated three different areas in northern California (fig. 68). The results of a quick field test for iodide sorption are given in figure 69. The iodide sorption by these volcanic soils ranged from 0 to 0.91 millequivalents per 100 grams of soil. The search for soils with higher sorption of iodide continues and after the survey is further along we will determine distribution coefficients of promising soils.

Tritium Migration Model

By D.E. Smiles, W.R. Gardner, *and* Robert K. Schulz

Tritium, when released as tritiated water at a point in a uniform and relatively dry soil, redistributes in both the liquid and vapor phases. The flux of tritium in each phase is of the same order of magnitude, however, so tritium redistribution must be modelled recognizing transfer "in parallel" in both phases.

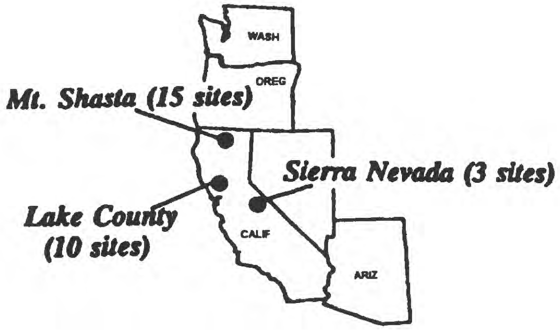

Figure 68. Sample locations.

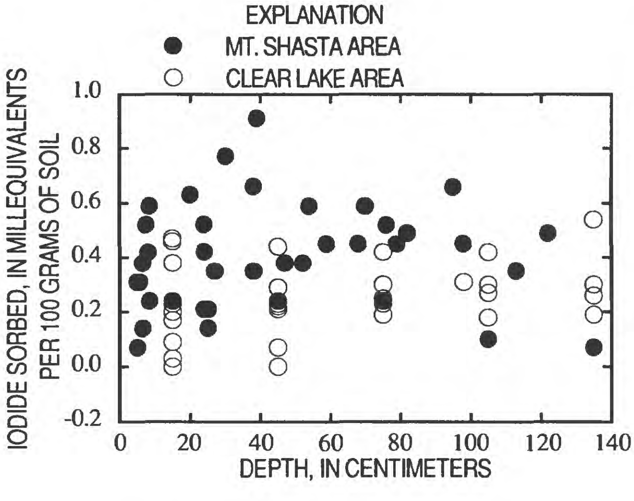

Figure 69. Iodide sorption by volcanic soils of northern California.

The diffusion equation cast in radial (spherical) coordinates, taking into account radioactive decay, may be used to analyze this problem. The analysis assumes that:

- HTO transfers as if it were water or water vapor, and that it is partitioned between the phases in proportion to the partitioning of water between the phases;
- Equilibrium exists at all times between tritium in the base and liquid phases;
- HTO undergoes radioactive decay with a half-life of 12.3 yr.
- The effective diffusion coefficient is in the order of 10^{-6} cm^2/sec.

The solution calculates the fate of tritium within and external to the sphere of released solution, assuming the initial concentration within this sphere to be uniform. Smiles and others (1993) illustrate the phenomenon by considering the advance of the tritium as a "wave" ahead of which the local concentration increases and behind which it decreases.

Figure 70 shows the way the tritium concentration, C, increases relatively rapidly and decreases slowly at radial distances r = 2, 4, 6, and 8 m from the release point. The maximum decreases with distance and advances virtually linearly with time.

It is important to note that the diffusivity was estimated by illustrative calculations described. It must be supported by field measurement when the theory is used for engineering application.

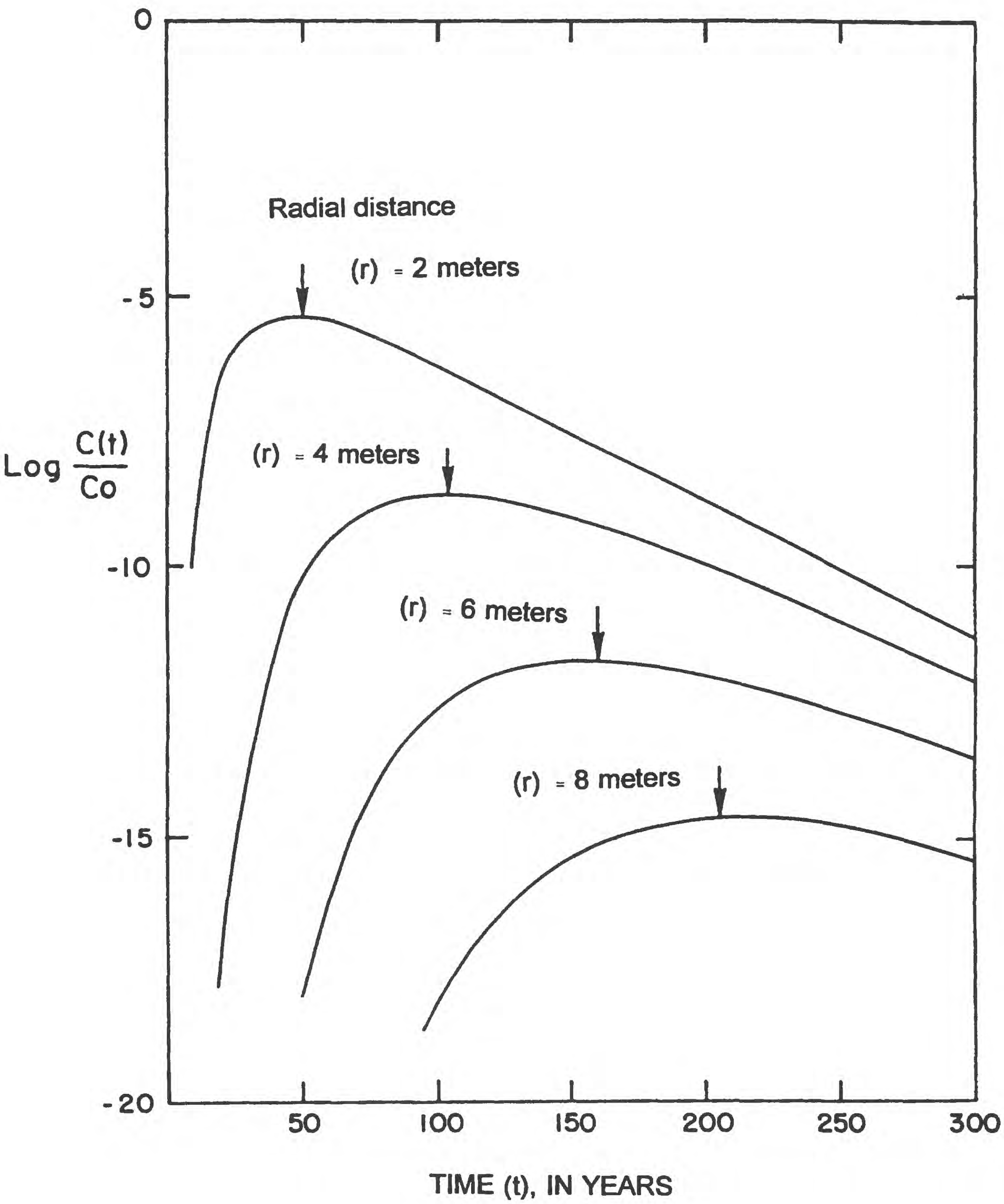

Figure 70. The way the tritium concentration C(t) changes with time at r = 2, 4, 6, and 8 meters from the point of release of the tritium. Note the apparently linear decrease in the logC(t)/Co_{max} with distance, and the linear advance of the maximum in time. Co is the initial axial concentration of tritium.

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TWO-DIMENSIONAL REACTIVE-FLOW MODELING OF URANIUM TRANSPORT IN PROTEROZOIC SEDIMENTARY BASINS

By Grant Garven *and* Jeff P. Raffensperger

Introduction

The study of uranium ore deposits as natural analogs for geologic repositories of nuclear waste requires a basic understanding of the hydrologic systems responsible for ore formation and subsequent periods of geochemical alteration. Although it is generally believed that the huge unconformity-type uranium deposits of the Athabasca Basin, northern Saskatchewan, Canada, and the McArthur Basin, Northern Territory, Australia, formed through the transport of uranium in hot, saline ground water (Hoeve and Sibbald, 1978; Hoeve and Quirt, 1984; Kyser and others, 1989), until now no study had examined the paleohydrology of ore formation nor examined the coupling between fluid flow, heat transport, and reactive solute transfer. The overall goal of this presentation is to discuss our progress in·quantifying the paleohydrology of Proterozoic sandstone basins through theoretical research, particularly as it relates to natural analogs (ore districts) in basins of northern Australia and Canada.

Methodology

Key issues concerning the paleohydrology of unconformity-type uranium deposits include the relationship between basin tectonics and flow systems, the factors controlling regional ground-water flow, the effects of fluid flow on the thermal regime, and the geochemical scenarios for ore mineralization and subsequent phases of alteration. To address these issues, we have developed a numerical model that solves the coupled equations of variable-density ground-water flow, heat transport, and multicomponent reactive solute transport (fig. 71). The hydrogeochemical model is based on the method of finite elements for ground-water flow, heat transport, and solute transport, and on the assumption of local chemical equilibrium between the aqueous phase and mineral phases within reactive porous media. Compilations of thermodynamic data are derived from the literature and the work of Sverjensky (oral commun.). Hydrogeologic parameters are based on geologic lithology and known ranges in the governing parameters for modern environments. Details concerning the numerical approach in modeling reactive flows in porous media are described by others, many of which apply simultaneous solution or sequential iteration methods (Walsh, and others, 1984; Liu and Narasimhan, 1989; Yeh and Tripathi, 1991). Our model is unique in its ability to efficiently solve variable-temperature, reactive-flow problems on a workstation using a predictor-corrector method (Raffensperger and Garven, 1991).

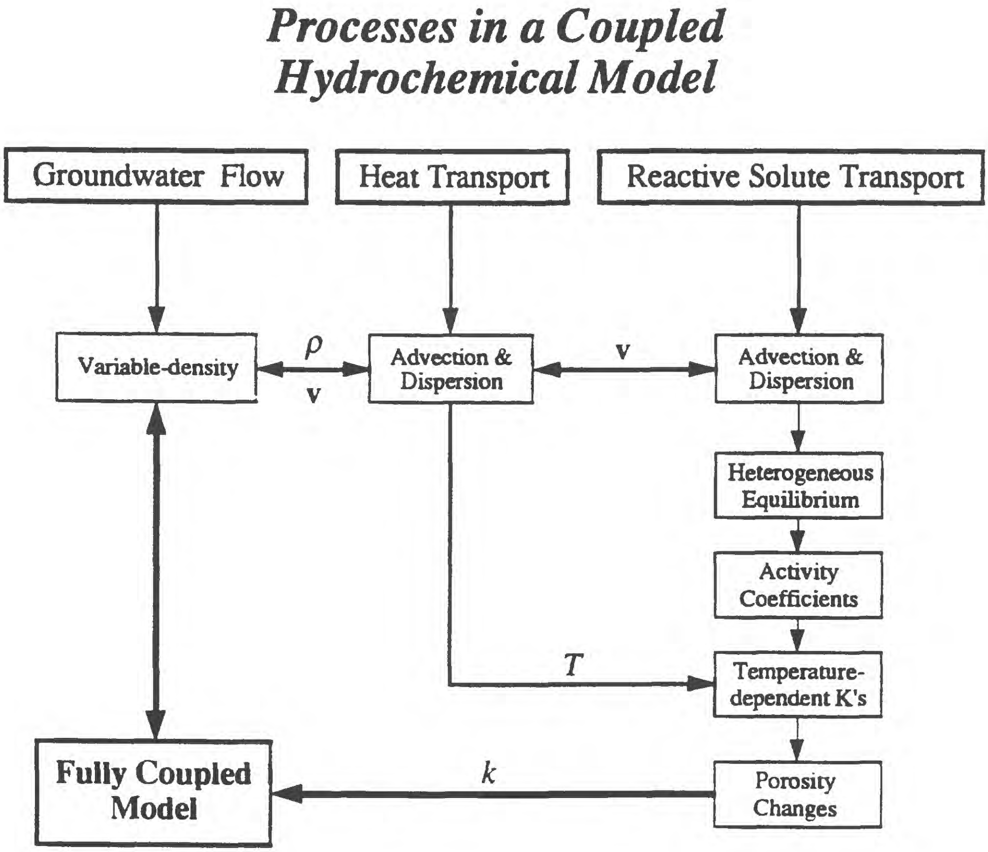
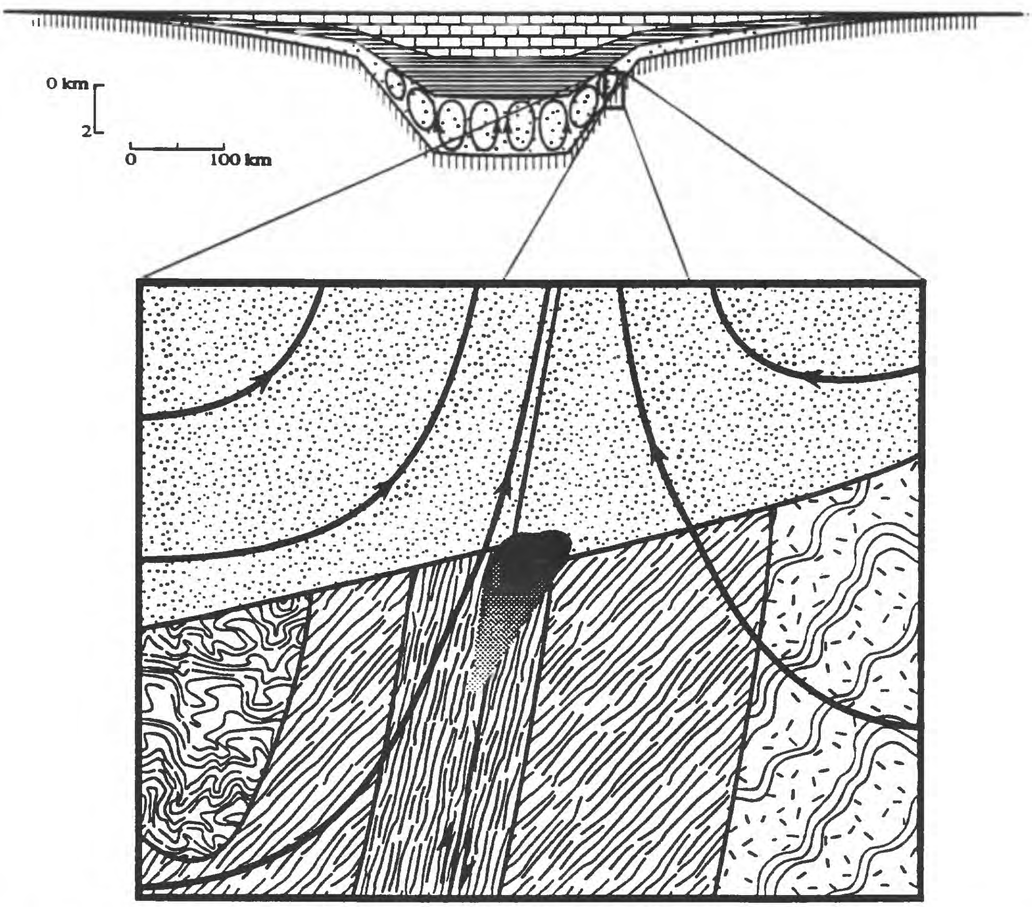


Figure 71. The organization of the coupled reactive-flow model. The symbols are as follows: T is temperature; v is ground-water velocity or flow rate; r is ground-water density; k is intrinsic permeability; and K is an equilibrium constant for chemical reaction. A finite element algorithm is used to solve the coupled flow-transport problems.

Some Preliminary Results

Our calculations presently are restricted to simulating two dimensional flow and transport along vertical cross sections through sedimentary basins (fig. 72). A major goal here is to apply the coupled transport model so as to define paleohydrologic conditions for uranium ore mineralization in large Proterozoic basins, thereby providing initial and boundary conditions on the far-field environment which can be used in repository performance assessment scenarios.

Results from dozens of paleohydrogeologic simulations of deep topography-driven ground-water flow and thermally-driven free convection suggest that both mechanisms were important agents for chemical mass transport in the Proterozoic sedimentary basins of northern Australia and Canada.



Conceptual Hydrothermal Model for the Origin of Unconformity-Type Uranium Deposits

Figure 72. Schematic section across a Proterozoic Basin showing the style of free convection driven by thermal gradients, along with an expanded view of the flow field near the unconformity between younger sandstone and older crystalline basement containing graphitic shear zones.

Simulations have been conducted for basin-scale (100-1,000 km) and regional-scale (1-10 km) hydrologic systems. Free convection probably played a more important role in primary ore mineralization, which later evolved to forms of mixed convection, and finally gravity-driven flow alone as the sedimentary basins were gradually uplifted by tectonic forces. Transport of fluids and heat along major fracture zones had an important role in ore formation, at least within the fractured metasedimentary basement. It should be noted that the simulations presented here are currently handicapped because we cannot portray the three-dimensional hydrology as might be required for a repository setting.

One smaller-scale two-dimensional flow simulation is described also to illustrate the potential application of the reactive-flow model in understanding geochemical scenarios of uranium mobilization in the near field, primary mineralization, and the formation of a redox front. The region modelled is a 6-km deep by 10-km wide box, with four units: a basement unit, a graphite zone, a sandstone aquifer unit, and an upper confining unit. Two hundred finite elements are used to discretize the flow domain. No-flow boundaries were assumed on all sides of the domain. A constant temperature of 20 °C is assigned to the top boundary and a basement heat flux of 80 mW/m^2 is assigned to the bottom boundary. The sandstone unit contained nearly all of the ground-water flow within the region caused by free convection because of the natural permeability contrast, with Darcy flow rates up to 0.5 m/yr. Flow is driven downward at the sides and upward at the domain center, above the more thermally conductive graphitic shear zone. Transport of multicomponent reactive solutes, subject to local equilibrium, is modeled also, including the precipitation of primary and secondary mineral phases. Fourteen chemical components are involved, including about 60 aqueous species and 10 minerals. About 25 hours of CPU time were required to run the FORTRAN code on an IBM RS/6000-560 workstation.

After simulating 500,000 yr of flow and transport, a large uranium ore body forms at the unconformity surface between the sandstone and graphitic basement. The source of the uranium is the far-field sandstone and uraninite is precipitated through reduction of uranyl and its complexes by methane generated from hydrothermal alteration of graphite. A stable redox front develops in the vicinity of ore deposition, while the carbonate concentration in the ground water increases well above the ore body due to the precipitation of ore. Without significant ground-water flow into the basement, less uraninite is deposited, and ore deposition near the unconformity is constrained by rates of diffusion of methane up from the graphitic zone. Significant transport of ground water must occur therefore through the basement metasediments, particularly through the graphitic shear zones which probably formed narrow paleoaquifers and focused hydrothermal ground water into basal sandstones. Time scales of 1 million years or more are required to concentrate the large ore bodies such as Jabiluka (230,000 tons) in the McArthur Basin and Cigar Lake (100,000 tons) in the Athabasca Basin.

Conclusions

The ramifications of the hydrogeologic setting to uranium migration and mineralization are being evaluated through transport simulations that account for coupled advection, dispersion, diffusion, aqueous reactions, and mineral dissolution and precipitation at pressure, temperature, and salinity conditions that are analogous to environments surrounding the far-field of a nuclear waste repository deep saturated zone.

Directions for future research include:

- Three-dimensional flow and transport modeling of paleohydrologic systems.
- Treatment of fracture networks within a porous-medium framework.
- Application to present-day analog sites to understand weathering processes.
- Expansion of the hydrochemical model to include reaction kinetics and isotopic fractionation.
- Stochastic treatment of permeability so as to better characterize uncertainty in model scenarios of mass transport.

The results presented here are preliminary, but clearly illustrate the utility of coupled, reactive-flow modeling in understanding paleo-conditions for mineralization. No other tool is available which has the ability to integrate geologic, hydrologic, and geochemical processes in a single assessment. Proper evaluation or characterization of subsurface data requires an integrated approach in performance assessment, as no single set of data alone (whether it be hydrologic or geochemical) can be used to independently understand mass transport in the near or far field without taking into account how processes overlap or affect each other. Our numerical model represents the type of new software available today which can be executed on workstations to better assess ancient, present-day, and future scenarios of chemical mass transport in the subsurface. Future performance assessment work on natural analogs as repository scenarios ought to make use of this frontier technology.

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DISPOSAL OF LOW-LEVEL RADIOACTIVE WASTE BELOW THE WATER TABLE—AN EXPERIMENT IN CLAY-RICH TILL AT WEST VALLEY, NEW YORK

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Introduction

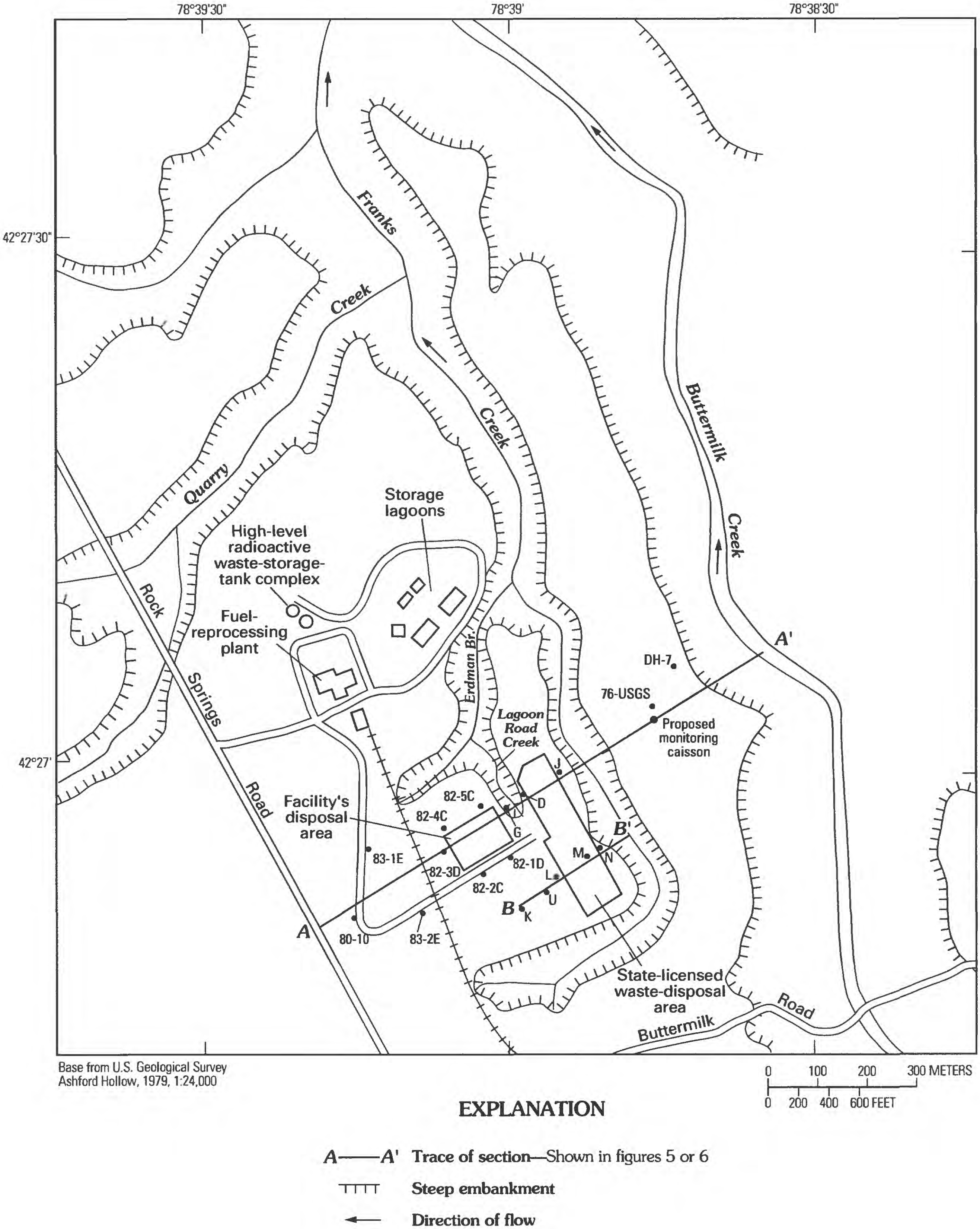
The Low-level Radioactive Waste Policy Amendments Act of 1986 requires that the low-level radioactive waste generated within each State be disposed of either within the borders of that State or in a host State under an interstate compact. Current methods of low-level radioactive waste disposal in the United States typically utilize shallow burial trenches. Geologic deposits in arid environments are considered good locations for these disposal sites because the lack of precipitation and the thick unsaturated zone in these areas limits the movement of water through the waste materials. However, it is likely that disposal sites will also be necessary in states located in humid areas.

Burial of low-level radioactive waste below the zone of weathering in saturated, fine-grained sediments is a disposal option that has been considered for humid areas where the abundance of precipitation precludes burial in the unsaturated zone. The use of this disposal option in the United States requires that a diffusion-dominated flow system persist for 500 yr to allow sufficient time for the principal radionuclides in the waste to decay to harmless levels. Several studies have characterized deposits of fine-grained sediments in which diffusion appears to be the dominant transport process (Keller and others, 1988; Desaulniers and others, 1981; Prudic, 1986). However, little information is available to indicate whether proposed burial methods will allow fractures to develop within the host material or the grout used to seal the excavation, thereby providing advective pathways connecting the waste to land surface.

In the proposed study a hollow steel cylinder (monitoring caisson) will be placed within an augered hole in clay-rich till to simulate a full-scale disposal facility, and the effects of excavating and sealing the facility on the movement of water through saturated, fine-grained sediments that serve as the host material will be investigated. The proposed study will consist of three components: (1) site characterization, (2) emplacement and operation of the monitoring caisson to simulate waste burial, and (3) site remediation. This paper briefly describes the approach and plan of study for the field experiment, including procedures designed to determine the depth of advective transport in the till and ascertain the effects of subsurface disposal on the integrity of the surrounding till and on the movement of pore water through the disturbed till and grout materials.

Site Description

The proposed study will be conducted in a thick, clay-rich till at the Western New York Nuclear Service Center (WNYNSC) near West Valley, New York (fig. 73), a site that has been well-documented by previous studies (for example, Prudic, 1986; Bergeron and others, 1986). The till at the proposed research site is the uppermost deposit in a 150 m-thick complex of glacial deposits composed of till, lacustrine, and outwash sediments (fig. 74). The till is unweathered at depths below 5 m and has a hydraulic conductivity of 2 to 6 x 10^{-10} m/s. The hydraulic conductivity is an order of magnitude higher near land surface where the till is weathered and contains oxidized fractures. Most of the water entering the weathered till flows laterally through fractures and animal burrows towards depressions and gullies. The remain-



Base from U.S. Geological Survey
Ashford Hollow, 1979, 1:24,000

Figure 73. Location of proposed research site at the Western New York Nuclear Service Center. (Modified from Bergeron and others, 1986.)

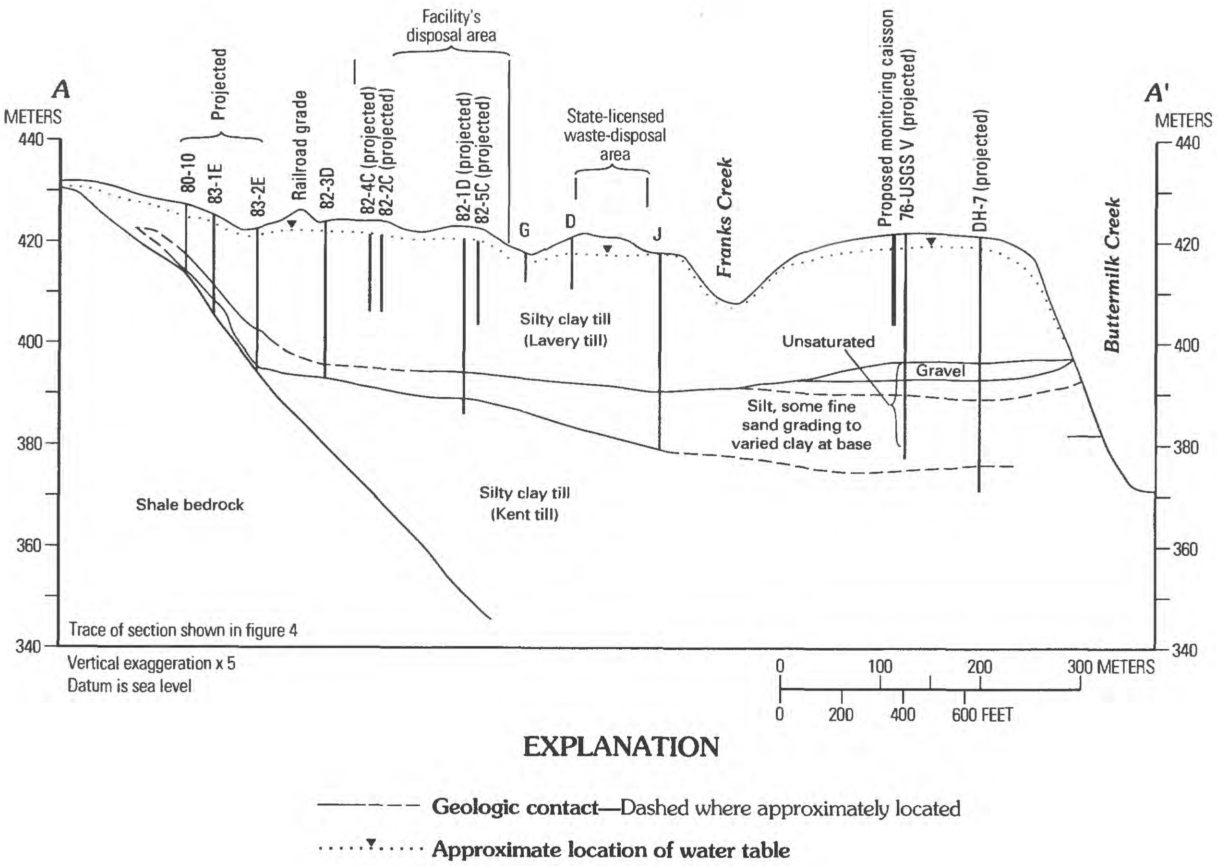


Figure 74. Major lithologic units. Location of section is shown on figure 73. (Modified from Bergeron and others, 1986.)

der enters the unweathered till and flows downward toward the underlying lacustrine sediments. The rate of flow through the unweathered till is estimated to range from 3 to 23 mm/yr.

Characterization of Till

Site characterization procedures will be conducted to determine physical and hydraulic properties of the till and to delineate zones dominated by advection and by diffusion within the till. Previous studies of clayey till deposits in Ontario have delineated a surficial, weathered zone 2 to 3 m deep in which fractures are abundant and readily visible because of staining from mineral deposition; at greater depths the till is unweathered and no fractures are discernible (Ruland and others, 1991). Ground water in the weathered zone has a chemical composition characteristic of recent recharge as a result of advective transport of solutes from land surface. Chemical concentration gradients at greater depths in the unweathered till suggest that water derived from meteoric water is mixing by diffusion with older water of glacial origin (Desaulniers and others, 1981; D'Astous and others, 1989).

The depth of advective transport, assumed to correspond to the depth of fracturing, will be determined through several methods, including direct observation of fractures in excavations, measurement of chemical concentration gradients along vertical profiles, and measurement of seasonal fluctuations in pore pressure in shutin piezometers using pressure transducers. Horizontal boreholes will be drilled through the sidewalls of research trenches at different depths in the till to intercept high-angle fractures in the till. Core samples obtained while drilling will be analyzed for tritium to detect recent recharge, indicating the presence of high-angle fractures that conduct infiltration from the land surface to depths below the weathered portion of the till.

The diffusion-dominated part of the flow system will be determined by comparing concentration gradients of ^{18}O and ^{2}H measured in the till to concentration gradients computed with the advection-dispersion and diffusion models to simulate the dilution of pro-glacial meltwater by post-glacial, meteoric waters. The rates of advective and diffusive transport estimated by the simulations will be compared to determine whether diffusion is the dominant transport process in the unweathered till.

Emplacement of Monitoring Caisson

The monitoring caisson will be 1.8 m in diameter and 20 m long and contain moveable steel platforms to provide access to different depths within the caisson (fig. 75). The annular space surrounding the monitoring caisson will be sealed with layers of three different grout mixtures selected on the basis of laboratory studies. Both cement and bentonite grouts will be used to determine the effects of grout composition on the sealing properties of the installation.

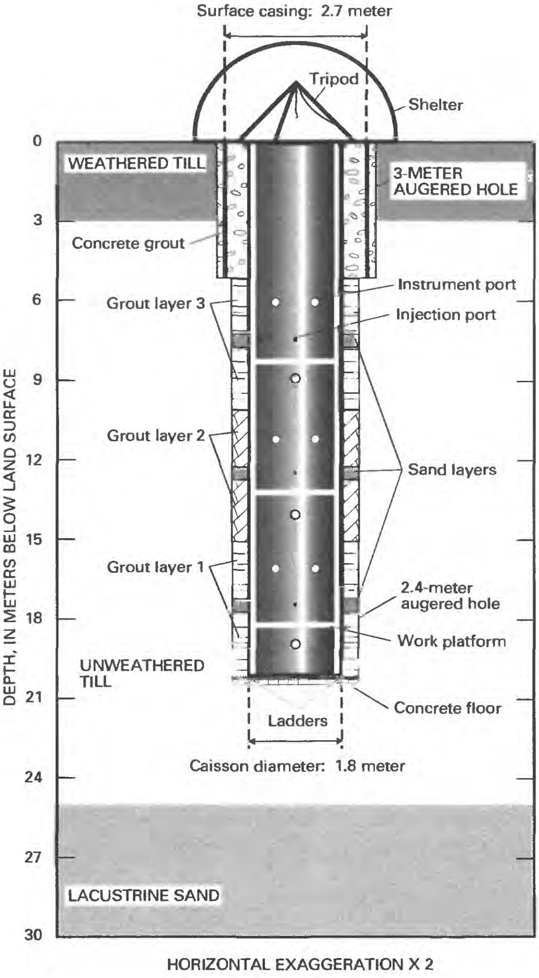


Figure 75. Proposed design of monitoring caisson.

A hydromechanical model will be developed to simulate changes in the state of stress in response to the excavation, emplacement and sealing of the monitoring caisson, and hydration of the grout. Model results will be used to design grout properties and determine the best locations for placement of monitoring points surrounding the caisson. Instruments placed in the annulus and surrounding till will record actual changes in the state of stress to verify the model results and monitor the hydration of the grout. Displacement in the till will be measured with slope indicators and a monument survey. Hydration of the cement grout will be monitored by strain gages, stress meters, thermocouples and pressure transducers. Saturation of bentonite grout will be monitored with stress meters, time-domain reflectometry probes, thermocouple psychrometers and pressure transducers. Other instruments will be placed in sand layers within the grout layers to measure pore pressure and detect solute migration during injection tests.

The interface between the till and grout is the most probable pathway of radionuclide migration from waste buried in augered holes in saturated sediments and sealing this interface is essential to maintain diffusion-dominated transport in the vicinity of a subsurface disposal facility (Vorauer and Chan, 1988). The upper limit of the hydraulic conductivity of the till/grout interface will be estimated through constant-head injection tests in which water is injected into the sand layer within each grout layer (fig. 76). The test results will be analyzed to determine which of the following flow conditions best represents the tests: (1) the grout is impermeable and radial flow occurs into the till, (2) the till is impermeable and axial flow occurs through the grout, or (3) both the till and the grout are impermeable and axial flow occurs through a gap at the till/grout interface (fig. 77). If flow is occurring along the till/grout interface (condition 3), the flow rate measured during the injection will be greater than one hundred milliliters per day, otherwise the flow rate will be in the range of tens of milliliters per day.

If the results of the injection tests indicate that flow is occurring along the till/grout interface, a tracer solution containing an electrically-conductive solute and dye will be injected into the sand layer to determine the location of the preferential flow path. Leak detection sensors that are triggered by the presence of a conductive fluid will be monitored during the test to locate the flow path. A coring tube will be driven through the area of suspected flow to obtain a sample of the till/grout interface for inspection and chemical analysis.

The potential for chemical alteration of till and grout in the interface region will be investigated by analyzing core samples obtained by drilling from the caisson wall through the grout and into the till. Pore water will be extracted from the core to determine the aqueous chemistry and thin slices of the core will be analyzed to determine the mineralogy of solid phases in the till and grout within the interfacial region. Previous studies have shown that differences in pH between clay and cement grout could result in precipitation and dissolution reactions involving calcite and calcium hydroxide (Jefferies and others, 1988) , and that ion exchange reactions involving sodium and calcium could affect the clay structure in the till and the bentonite grout (Sawyer and Daemen, 1987).

Benefits of Study

The proposed study will investigate processes affecting the sealing performance of grouts in glacial till in a large-diameter (2.4 m) borehole, similar to those used by Ontario Hydro to store low- and intermediate-level radioactive waste in Canada. Previous studies have investigated processes that control the sealing performance of grouts in different materials and in boreholes smaller in diameter than the augered borehole proposed for this study. Laboratory and field studies have assessed the sealing performance of cement and bentonite grouts in 2.5 to 10 cm diameter boreholes drilled in recrystallized limestone (Greer and Daemen, 1991) and volcanic tuff (Ouyang and Deamen, 1992). Cement grout was used to seal a 91.4 cm diameter borehole in halite at the Waste Isola-

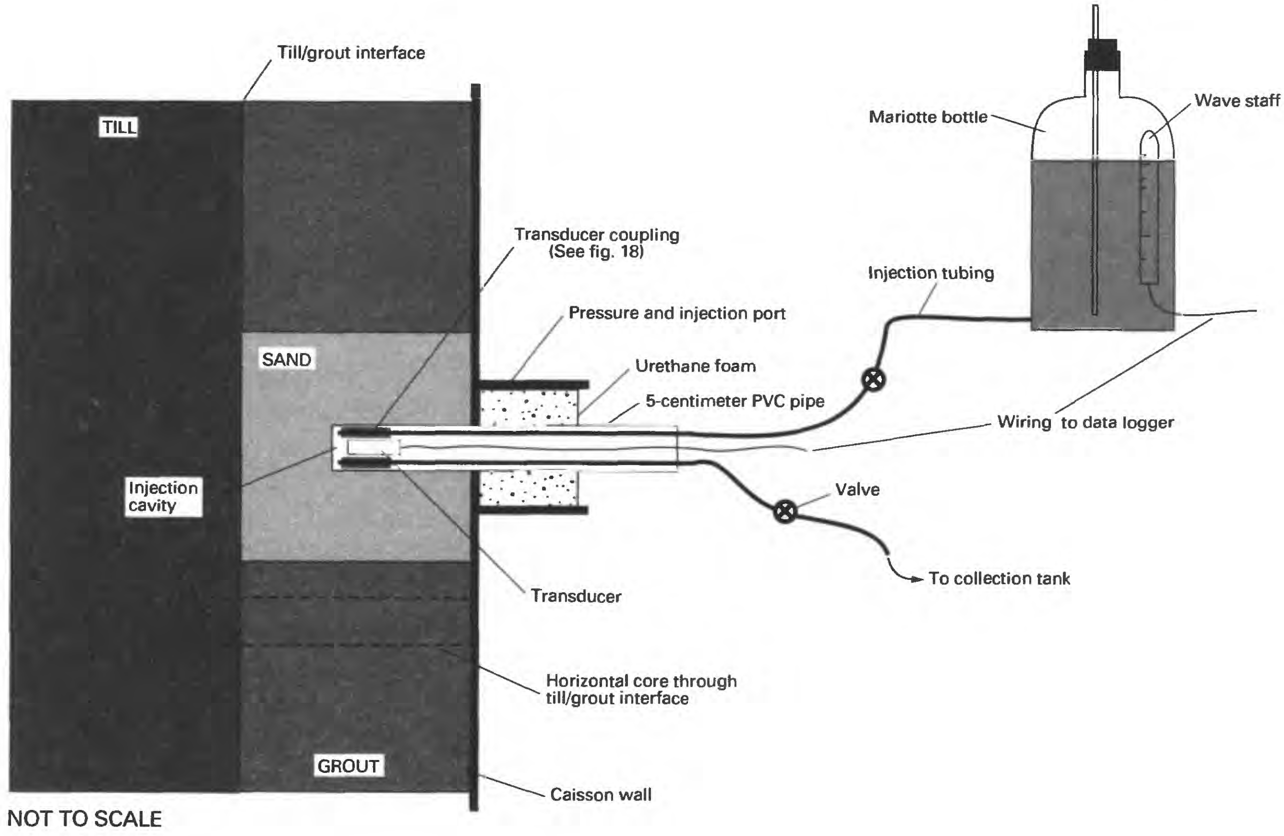


Figure 76. Equipment for conducting injection tests of till/grout interface.

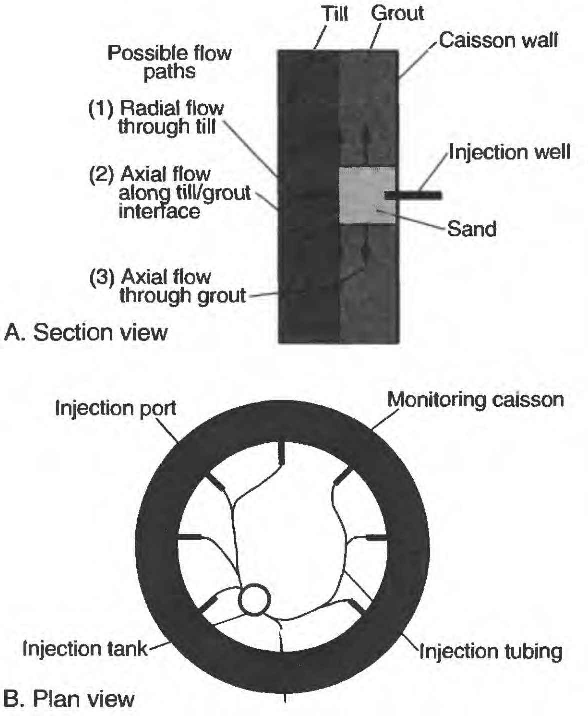


Figure 77. Possible flowpaths in injection tests of till/grout interface.

tion Pilot Plant in New Mexico (Stormont, 1986), and bentonite grout was used to seal a 124 cm diameter borehole in granitic rock at the Underground Research Laboratory in Manitoba (Kjartanson and others, 1991). Construction of the monitoring caisson proposed in this study will allow testing of a full-scale facility for an extended period of time, so that the long-term effects of mechanical, hydraulic and chemical processes on water movement can be investigated.

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