

ORNL/TM--11463

DE91 001013

Environmental Sciences Division

DESIGN OF A FIELD EXPERIMENT FOR
INJECTION OF NATURAL COLLOIDS IN A SANDY COASTAL PLAIN AQUIFER,
BELLE W. BARUCH FOREST SCIENCE INSTITUTE, GEORGETOWN, SOUTH CAROLINA

L. E. Toran, J. F. McCarthy, and T. M. Williams*

*Belle W. Baruch Forest Science Institute, Clemson University,
P. O. Box 596, Georgetown, SC 29442

Environmental Sciences Division
Publication No. 3455

Date Published -- June 1990

Prepared for the
Office of Energy Research

Budget Activity KP 02 03 00 0

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6285
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

MASTER

EB

CONTENTS

	<u>Page</u>
LIST OF TABLES	v
LIST OF FIGURES	vii
EXECUTIVE SUMMARY	ix
1. INTRODUCTION	1
2. OVERVIEW OF RESEARCH PROJECT	1
2.1 HYPOTHESES	2
2.2 RELATED PROJECT RESEARCH	2
3. PURPOSE OF THE FIELD INJECTION EXPERIMENT	3
4. SITE DESCRIPTION	5
5. PERMIT RESTRICTIONS	11
6. DESIGN OF INJECTION EXPERIMENT	14
6.1 INJECTION SOLUTION	14
6.2 DRILLING METHOD	15
6.3 WELL CONSTRUCTION	15
6.4 INJECTION AND WITHDRAWAL PUMP	18
6.5 HOLDING TANK	18
6.6 FIELD SAMPLING FOR COLLOIDS AND OTHER GEOCHEMICAL PARAMETERS	18
6.7 SAMPLING SCHEME	21
6.8 PHASE I: FORCED GRADIENT	21
6.8.1 WELL ARRAY	21
6.8.2 INJECTION RATE	25
6.8.3 SERIES OF FORCED GRADIENT EXPERIMENTS	25
6.9 Phase II: NATURAL GRADIENT EXPERIMENT	25
6.9.1 WELL ARRAY	25
6.9.2 INJECTION RATE	29
APPENDIX A: SUMMARY OF INJECTION PLAN REVIEW	31
A.1 AGENDA FOR MEETING WITH REVIEWERS	33
A.2 ATTENDEES AND REVIEWERS	35
A.3 SUMMARY OF CHANGES SUGGESTED BY REVIEWERS	36
APPENDIX B: RESULTS OF CHLORIDE TRACER TEST	37
B.1 FIRST STAGE	39
B.2 NEXT STAGES	45

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Summary of background information	6
2	Summary of data from 21 Hobcaw Field Cores.	13
3	Comparison of fractionation of chlorinated and nonchlorinated Colloidal organic matter	16
4	Proposed sampling summary	20
5	List of experiments for first injection well site	27
B-1	Dispersion and velocity calculation from CXTFIT, a least-squares curve-fitting model.	43

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Hobcaw Field	7
2	Water levels and precipitation data through time	8
3	Water table map.	9
4	Water levels and precipitation data through time for a well cluster.	10
5	Total organic carbon concentrations through time	12
6	Well construction diagram.	17
7	Sampling system.	19
8	Modeled Cl breakthrough.	22
9	Modeled collidal organic matter breakthrough	23
10	Forced gradient well array	24
11	Forced gradient drawdowns in centimeters	26
B.1	Field site for forced gradient experiment.	41
B.2	Water level measurement in multi-level monitoring well	42
B.3	Measured and modeled breakthrough.	44

EXECUTIVE SUMMARY

Colloids may enhance contaminant transport by mobilizing chemicals that are generally thought to be immobile because they attach to solid surfaces. However, few data are available on the rate of colloid transport on a field scale or on demonstration of the fundamental chemical and hydrologic factors controlling colloid mobility. Thus, the potential for colloid-assisted contaminant transport is poorly understood at present. We are developing a field-scale experiment to examine colloid transport by injecting colloidal organic matter (COM) into a sandy aquifer at the Baruch Forest Science Institute in Georgetown, South Carolina. We will trace the movement of the colloids along a known flow path and examine chemical and hydrologic influences.

The first step in designing the colloid injection experiment was to conduct a test with a conservative tracer, KCl. The purpose of the chloride injection was to determine field values for groundwater velocities and dispersivities, to test monitoring equipment, and to determine feasible injection rates. A 4-d experiment was conducted, in which 800 gal of KCl solution was injected and cycled through the sandy aquifer under a forced gradient with the use of an injection-withdrawal well pair spaced 5 m apart. The chloride tracer was monitored in the groundwater at two monitoring wells, spaced at 1.5 and 3 m from the injection well. Each monitoring well had 11 sample ports spaced at 0.15-m depth intervals. In all, approximately 600 samples were collected and analyzed for chloride over the 4-d period.

The breakthrough curves of chloride showed at least three different velocity zones with depth. These three zones will form the focus of later experiments and could not be predicted without the chloride tracer experiment. Sequential breakthrough was observed at the two monitoring wells, indicating connectivity over the scale of the experiment. The field values of velocity and dispersivity will be used to refine projections of COM mobility and sampling rates needed for design of that experiment. The different velocity zones provide a contrast in hydrologic conditions that can be used to test the relative influence of hydrologic vs geochemical factors in COM transport.

1. INTRODUCTION

This report summarizes the design of field injection experiments that constitute one task in the larger project described in the report "Experiments Using Natural Organics." In the experiments, we plan to inject a large volume of colloidal organic matter (COM) into a sandy, unconsolidated coastal aquifer and observe the migration of COM into the groundwater flow system. The report provides a brief overview of the research project, including hypotheses to be tested; describes the purpose of the field injection experiments; summarizes the site characterization preliminary to the experiments; and explains the design of the experiments.

The first draft of this report was reviewed in detail by experts in hydrogeology, colloid sampling, and field injection experiments (see list, Appendix A). After receiving written comments from reviewers, a small group of experts met with project personnel at the field site in South Carolina to discuss plans for the experiments in more detail. This revised plan reflects the recommendations and insights of these reviews, summarized in part in Appendix A.

2. OVERVIEW OF RESEARCH PROJECT

The mobility of a contaminant depends on the relative affinity of the chemical for binding to an immobile phase (aquifer material) or remaining in the mobile phase. Chemicals with a high affinity for binding to surfaces of aquifer material are therefore assumed to have limited mobility. However, aquifers may also contain organic and inorganic colloidal material that is transported through the aquifer in the mobile phase. This project seeks to understand the potential role of COM in the subsurface transport of organic contaminants. The research includes both laboratory characterization of colloid interactions and field injection experiments. In the field experiments, a slug of COM will be injected into a shallow aquifer, and plume development will be monitored.

Although there is circumstantial evidence, based on observations of enhanced contaminant transport, that colloids are mobile in the subsurface environment, little data are available that demonstrate that rate of colloid transport on a field scale or that describe the chemical and hydrological factors controlling colloid mobility. Controlled studies in the field are needed to confirm that colloids are mobile and to provide understanding of the fundamental mechanisms controlling the mobilization and deposition of colloidal material.

The surface characteristics of both colloids and aquifer material are a key factor in determining the nature and magnitude of chemical interactions that control the mobilization and deposition of colloidal particles. Natural COM is a heterogeneous mixture of organic

macromolecules containing a diversity of functional groups and differing in size, charge, and hydrophobicity. Thus, different components of natural COM might be expected to display a range of chemical interactions with aquifer solids. Certain subcomponents of natural COM might be significantly mobile, while more reactive components will be retarded. An understanding of the selective retention, or chemical fractionation, of COM migrating through an aquifer can provide information to help predict how chemical heterogeneity affects transport. In contrast to these chemical factors is the structural and textural heterogeneity of the subsurface environment, which may provide channels for colloid mobility. For example, fractures have a smaller surface area for reaction than pores do and may obscure fractionation processes. Other hydrologic features that need to be considered include differences in flow rate, grain size, and permeability. Very little is understood about the role of hydrologic factors on colloid transport, especially in natural systems.

2.1 HYPOTHESES

Specific hypotheses to be tested in this project include the following:

1. Colloid transport will be enhanced by increased groundwater flow rate and by large-scale physical, chemical, or mineralogic heterogeneities; transport will be attenuated by clay, ironoxides, and solid organic matter, where present.
2. COM will be mobile in groundwater, both as discrete solutes and as organomineral complexes; COM will mobilize mineral particles by electrochemically stabilizing them in suspension in groundwater.
3. Mobile allochthonous (injected) organic matter will be retarded due to binding to aquifer media, but some subcomponents of the COM will have a much greater potential for sorbing to aquifer material; there will be preferential loss of the more electronegative and hydrophobic subcomponents of the allochthonous (injected) organic material in the mobile phase.
4. Colloid transport through an aquifer will depend on the spatial distribution of controlling chemical, hydrologic, and mineralogic properties of the formation; transport can be predicted from a geostatistical description of the spatial dependency of these parameters.

2.2 RELATED PROJECT RESEARCH

The project includes an extensive laboratory study of the chemistry of the injected stream COM, sorption properties referenced to the site

aquifer material, and pollutant interactions. The laboratory studies provide a theoretical basis for interpreting field data, while the field studies will be a test of the ability of laboratory experiments to make predictions on a field scale. Both laboratory and field data will be used in computer models to test whether colloids can be modeled as solutes or whether new parameters or models are needed to describe colloid transport.

3. PURPOSE OF THE FIELD INJECTION EXPERIMENT

The purpose of this field injection experiment is to determine (1) whether COM that binds contaminants is mobile in subsurface environments, (2) its rate of mobility, and (3) whether its mobility can be predicted based on sorption properties, hydrologic properties, and groundwater flow rates. In the simplest terms, by injecting a large volume of water from a stream containing a high concentration of organic matter, we will find out if organic colloids can be transported through a sandy, porous aquifer. In the course of the experiments, we also expect to find out about the presence and mobility of autochthonous (preexisting in the groundwater) inorganic and organic colloids. Specifically, the following questions will be addressed: Will colloids be mobile in a sandy aquifer? What sorption properties and flow rates influence the mobility of colloids, how will these factors interact, and how will these be manifested in a heterogeneous, natural system?

Thus, the objectives of this field injection experiment task are to demonstrate, as a proof-of-principle, that colloids are mobile on a field scale and to develop field data to test and extend our laboratory-derived understanding of fundamental chemical and hydrologic processes that control colloid transport. This field experiment is complemented by laboratory research to determine the relative influence of physical and chemical phenomena in the mobilization and deposition of colloids. This combination of lab and field information can be used to develop the capability to predict the extent of mobilization of colloidal particles and the role of colloids on the transport of groundwater contaminants.

The mobility of colloids, not just their presence, must be determined. The field injection experiment will provide a unique opportunity to characterize the mobile fraction of colloidal matter (as opposed to that merely collected in solution) by following a tracer plume along an observed flow path. The composition of injected water will be known, so the immobile fraction can also be determined.

We plan to do a series of forced gradient injection experiments followed by a long-term natural gradient injection experiment. Thus, the field injection experiments are divided into two phases. Phase I focuses on forced gradient experiments, while Phase II will introduce natural gradient experiments.

The forced gradient experiments are an important first step in understanding the system and obtaining preliminary information about colloid transport hypotheses, including the following considerations:

1. Does the COM move, i.e., what is the soundness of mobility hypothesis? (Hypothesis 1)
2. By varying the hydraulic gradient, what is the resultant influence of flow rate on transport of both native and injected colloids? (Hypothesis 1)
3. What is the influence of the chemical, mineralogic, and hydrologic character of the aquifer on mobility and retention under forced gradient? (Hypothesis 4)

In addition, information from the forced gradient experiment will aid design of a natural gradient experiment by enhancing our understanding of factors such as the following:

- preliminary hydrologic parameters (dispersion coefficient, retardation, and retention) under forced gradients;
- testing and optimization of sampling techniques;
- injection rates; and
- detection limit for monitoring injected COM.

The detection ability for injected COM may be enhanced if the injection water can be chlorinated (discussed further in Sect. 5). The halogenated organic carbon (TOX) will provide lower detection limits and can be distinguished from autochthonous (native) organic carbon. This procedure will be tested in the forced gradient experiments, if it is allowed under the state permit.

A larger-scale natural gradient experiment is needed to obtain additional information concerning

- more realistic hydrologic conditions,
- hydrologic parameters under natural gradients (Hypothesis 4),
- "natural" retention and mobilization processes (Hypotheses 1 and 3), and
- influence of spatial variability of aquifer material (Hypothesis 4).

4. SITE DESCRIPTION

The proposed injection site is an abandoned farm field on the western side of the Belle W. Baruch Forest Science Institute, Georgetown County, South Carolina. The Institute is a research station for Clemson University and the University of South Carolina.

The injection water will be obtained from a forested stream on the site. The stream has 30 to 50 mg/L total organic carbon (TOC), such as natural humic and fulvic substances (Table 1). Pesticide use is restricted on the site, which eliminates anthropogenic sources of organic contaminants in the aquifer.

A summary of background information on the site and available chemical data (Table 1) indicates the site is moderately well characterized and meets several criteria necessary for a large-scale field experiment:

1. relatively high permeability and porosity;
2. low background concentrations of organic matter on aquifer material and in groundwater;
3. shallow water table; and
4. easy accessibility for drilling and sampling equipment, but protection from intruders or disturbances.

In addition to background information on the field station, 23 piezometers have been installed on the 1-acre field that will be the site of the injection experiments (Fig. 1). The water level in these piezometers was monitored for 4 months (Fig. 2). Fifteen wells were drilled to 10 ft and show fairly steady horizontal gradients (Fig. 3, 0.005 to 0.009) and recharge response (Fig. 2). Three well clusters were installed to look at vertical gradients with piezometers (labeled P in Fig. 1) at 5, 10, and 15 ft (Fig. 4). The upper two piezometers (P1, 2) in the cluster in the southeast corner of the field (upper end of water table) show a downward gradient (0.05). The water level in third piezometer in this cluster was periodically depressed by sampling, which obscured the natural gradient. However, initially it appears that there is recharge (a downward gradient) in this area, with a laterally conductive zone in the central piezometer (P2), which has a lower head than the bottom piezometer. The top and bottom piezometers (P4, 6) of the center cluster (middle of water table) show no recharge or discharge. The water levels in the middle piezometer of this cluster have been obscured by sampling and eventually caved in because of overpumping. The northwest cluster (lower end of the water table) shows discharge gradients (P7, 8), although the data are somewhat irregular due to sampling inconsistencies. Samples have been collected periodically to monitor TOC in the piezometers, and the

Table 1. Summary of Background Information

Hydraulic conductivity	0.01 cm/s average of 40 permeameter tests on core, additional slug tests and permeameter measurements in progress
Natural gradient	0.006 elsewhere on the field station, 0.001 to 0.009 Hobcaw field, natural gradient site
Geology	25-ft-thick sand layer bounded by clay layer at the base (Fig. 1); iron-rich (red) and iron-poor (grey) zones have been identified; texture is sand-clay mixture with rough (not rounded) grains <1 mm in size
Depth to water	1 to 5 ft
Geography	7.5-acre field, monitoring 100- by 400-ft ² portion (1 acre)
Topography	Less than 5 ft of relief from the center of the field to streams on the edge
Groundwater chemistry	Usually <3 ppm total organic carbon groundwater, usually <10 ppm Cl in groundwater
Stream colloidal organic matter	70% hydrophobic (50% hydrophobic acid, 20% hydrophobic-neutral), 30% hydrophilic, description determined by XAD-8 fractionations
Retardation factors	40 to 400, approximated from linearized K _d 's from laboratory isotherms between stream colloidal organic matter and Hobcaw field aquifer material

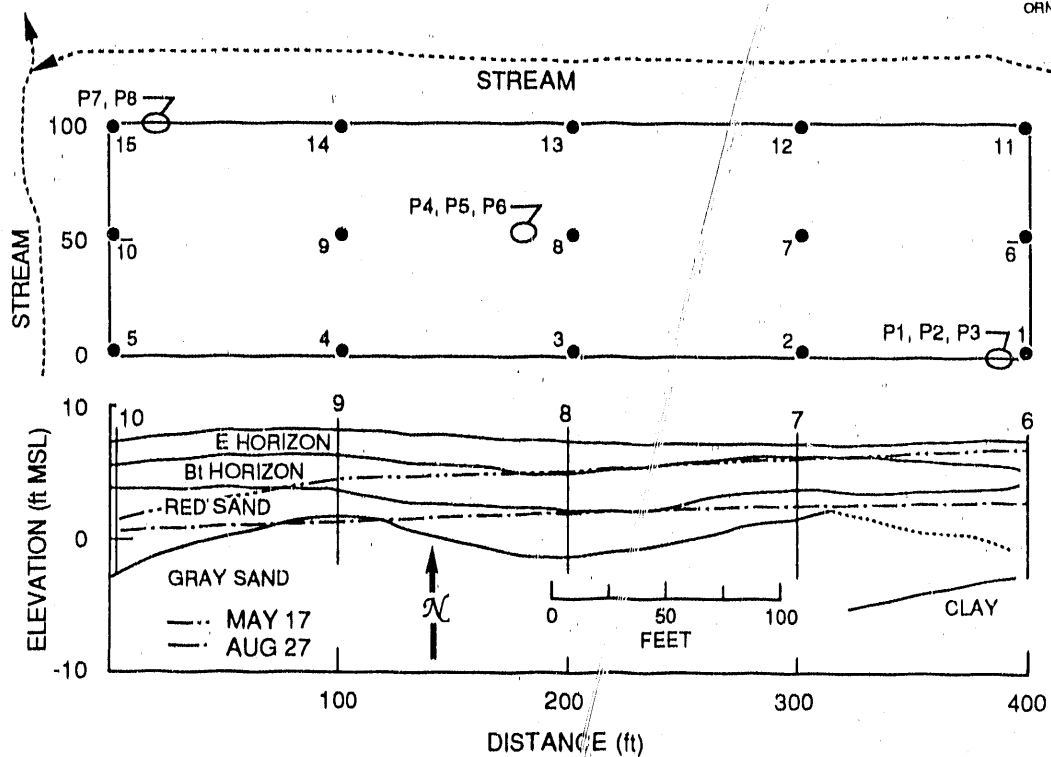


Fig. 1. Hobcaw Field: location of monitoring wells and cross section through centerline of wells. Numbers are well numbers; P's are nested piezometer numbers.

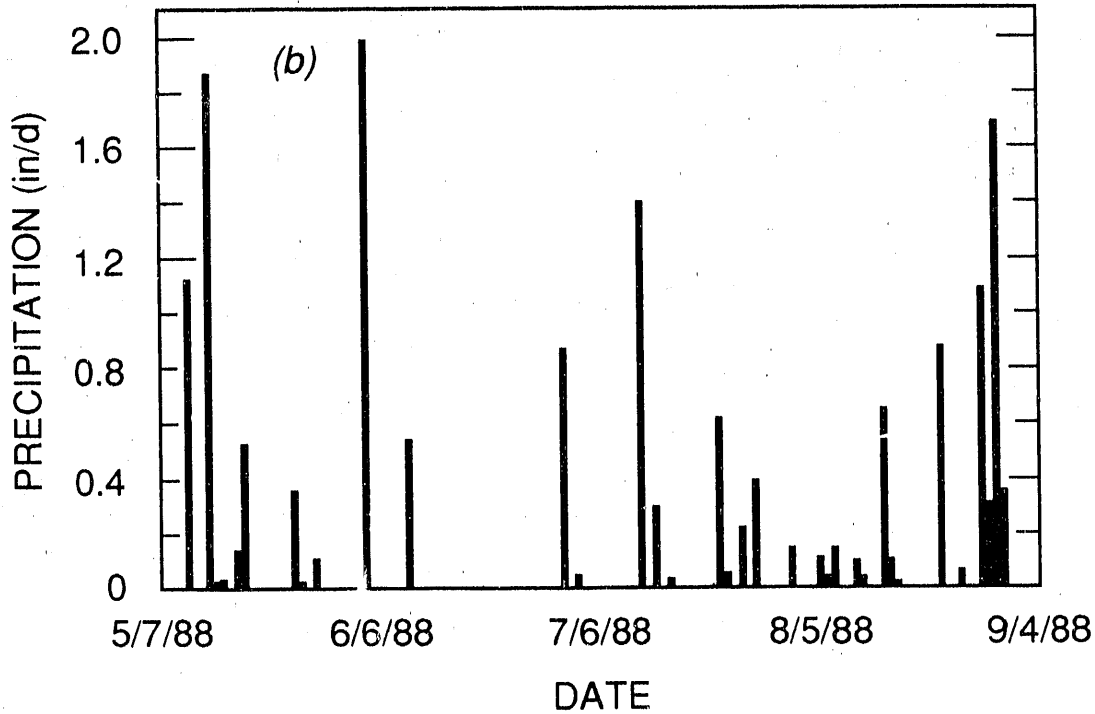
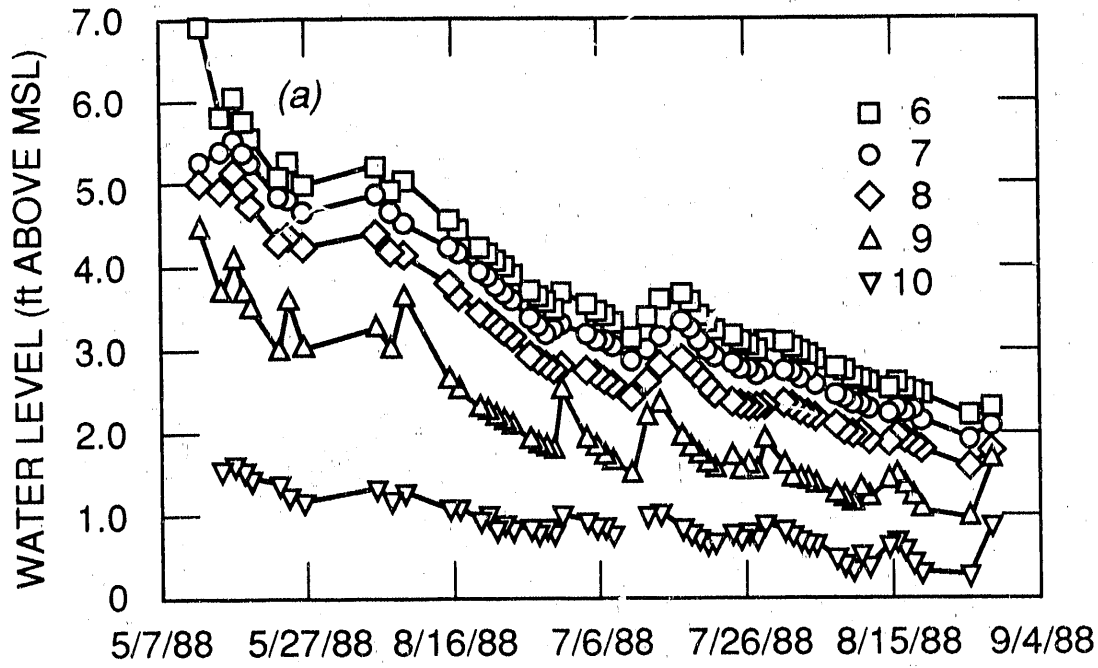


Fig. 2. (a) Water levels and (b) precipitation data through time for centerline of wells. Water levels show response to precipitation events.

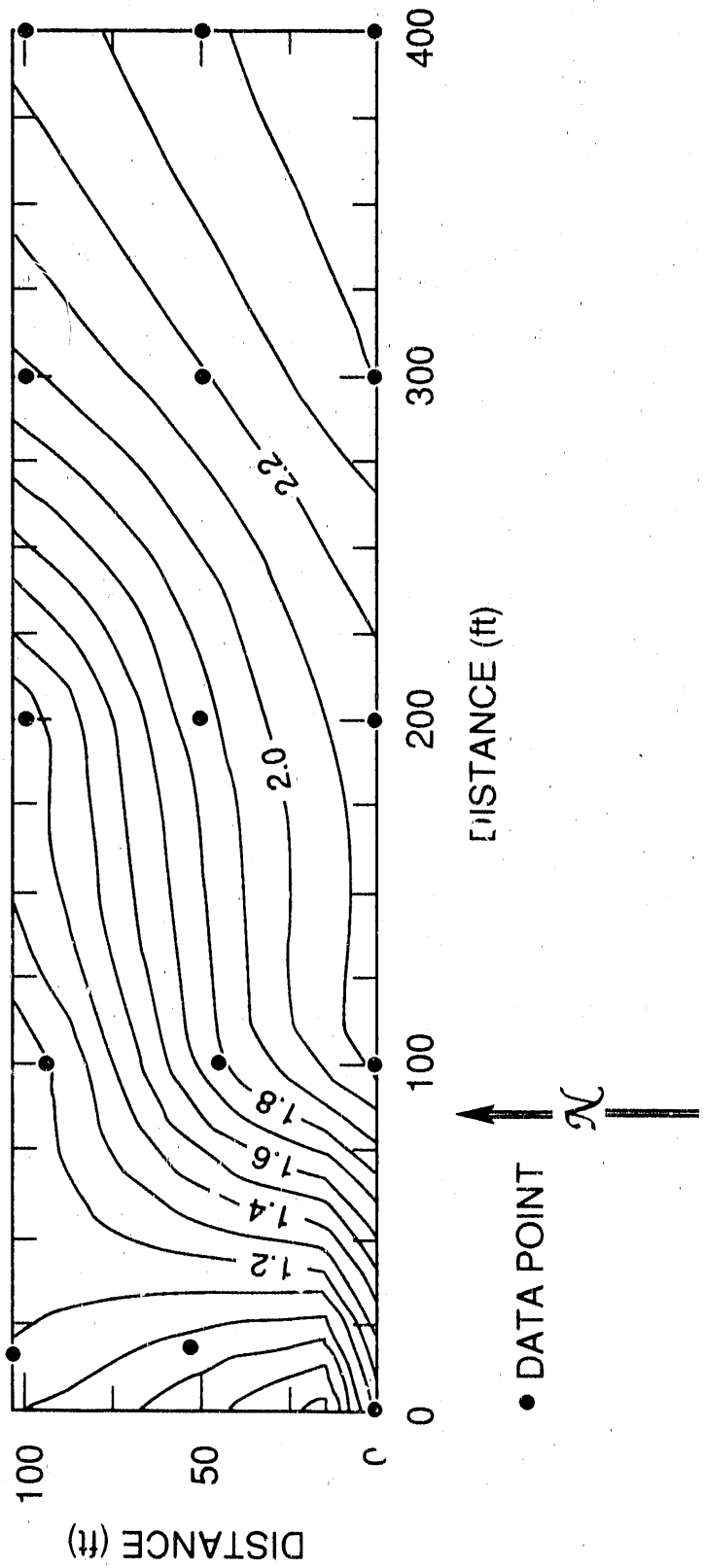


Fig. 3. Water table map for Aug. 26, 1988, in feet above mean sea level.

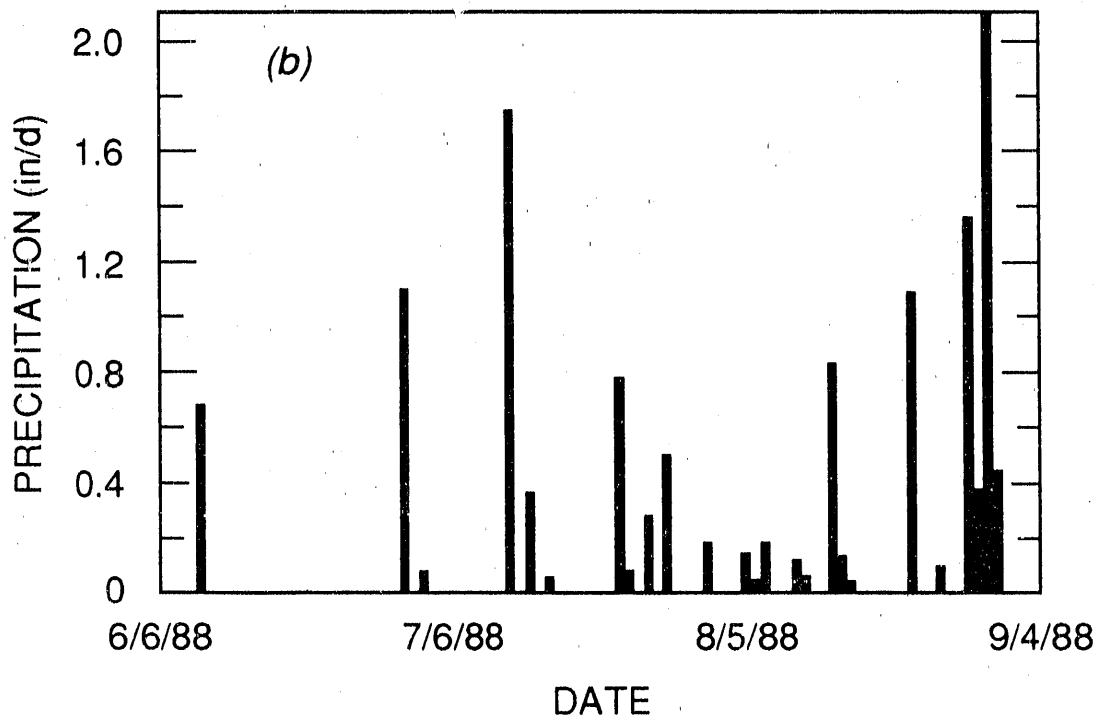
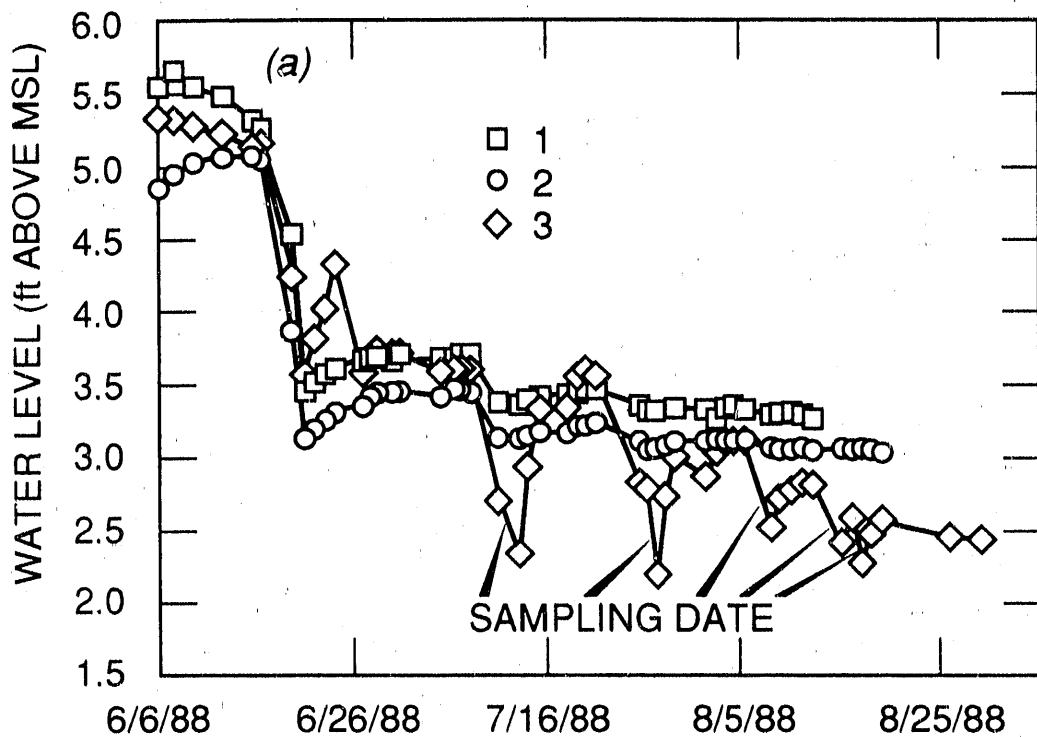


Fig. 4. (a) Water levels and (b) precipitation data through time for well cluster (piezometers 1-3).

concentrations were low (<10 mg/L as carbon and generally <1 mg/L). The concentrations are not steady through time (e.g., 0.3 to 3 mg/L as carbon, Fig. 5), but no special care was taken to assure colloid stability during this sampling.

Intact cores were collected at 20 locations in between each well in the field to provide spatial information on chemical, physical, and mineralogical properties of the medium. This information includes particle-size analysis, TOC content, total iron oxides, and hydraulic conductivity (Table 2). The cores have been segmented, so that the data are collected in a three-dimensional pattern. The chemical data are from core segments of 30- to 60-cm length, three to four per core. The hydraulic conductivities were measured on 25-cm segments, 4 to 11 per core. Data analyzed thus far show that the particulate organic carbon content is low (0.02 to 0.1%), and the iron oxide content is variable (0.3 to 28 mg/g). The mean value of hydraulic conductivity from approximately 20-cm-long segments in three cores was 0.006 cm/s. The values range from 0.0005 to 0.02 cm/s, indicating some variability. Variability was greater within the three cores than between them.

5. PERMIT RESTRICTIONS

The injection permit issued by the state of South Carolina contains the following restrictions of note.

1. Injection water must meet state drinking water standards, and analyses of the injection water taken during the experiments must be submitted to the state. Drinking water restrictions include coliform bacteria counts less than or equal to one colony per 100 mL.
2. The injection water may contain up to 100 mg/L Cl and 20 mg/L Br.
3. No more than 13 injection wells can be used.
4. The injections will total 15,000 to 25,000 gal, and larger volumes should probably be reevaluated by state officials.
5. The wells must be grouted at the surface and inspected by the state after drilling.

The injection permit has no expiration date.

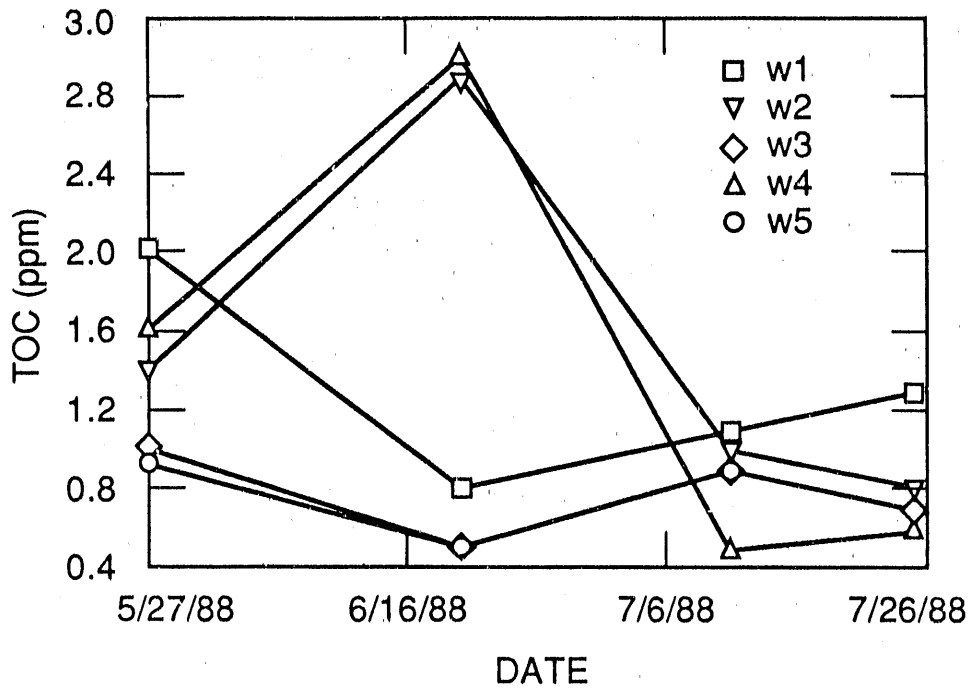


Fig. 5. Total organic carbon (TOC) concentration in milligrams of carbon per liter through time for south line of wells (1-5).

Table 2. Summary of data from 21 Hobcaw Field Cores^a

VARIABLE	RANGE OF VALUES
Sand (%)	83-95
Clay (%)	1.7-13.4
Silt (%)	0.3-5.6
Organic carbon (%)	0.02-0.1
Fe (mg/g)	0.3-28
Hydraulic conductivity (cm/s)	0.0005-0.02

^aSummary provided by P. M. Jardine.

6. DESIGN OF INJECTION EXPERIMENT

Except for the arrangement of the wells and the time frame, most design features are common to both phases of the experiments: the Phase I forced gradient experiments and the Phase II natural gradient experiment. These common features are first discussed, while the final sections (Sects. 6.8 and 6.9) address well arrays and injection rates for each phase.

6.1 INJECTION SOLUTION

The injection water (from a forest stream at the Baruch Forest Science Institute) contains 30 to 50 mg C/L TOC. The groundwater concentrations are ~1 mg/L, but some have been observed as high as 10 mg/L. There is no method for concentrating the injection water without fractionating the COM.

With this small contrast between injection water and background water, detection may be a serious problem. We plan to use "continuous" (i.e., long-term) injections for both the forced gradient and natural gradient experiments to try to overcome the concentration limitation. The site has been equipped with a 20,000-gal holding tank for injection water. The injection water will be monitored periodically through the course of the injections to check for stability of TOC concentration, number of E. coli, and possible changes in water chemistry.

Additional considerations regarding the composition of the injection water are as follows:

1. The presence of E. coli fecal coliform bacteria in the stream water would violate our injection permit, which stipulates that the injection solution meet the state's drinking water standard of one colony per 100 mL. Stream water sampled in April 1988 and January 1989 had coliform levels tenfold above this standard.
2. The injection wells could clog due to growth of subsurface microbial colonies that use the COM as a substrate.
3. Valuable new information could be obtained on colloid mobilization and transport if autochthonous (native) COM and allochthonous (injected) COM are differentiated.

Each of these points could be addressed by chlorinating the injection solution, a process which would kill bacteria, and then labeling the injected COM with chlorine. Preliminary data indicate no significant difference between fractionation of the chlorinated and nonchlorinated COM, so the injection solution would still contain a mixture of

hydrophilic and hydrophobic components (Table 3). Furthermore, no significant difference was observed between an isotherm describing interaction of COM and Hobcaw field aquifer material for chlorinated and nonchlorinated COM. By chlorinating the humic solutions at a low pH (approximately 4) and low ratios of NaOCl to carbon (2:1 or lower), the production of volatile organics can be minimized. The chlorinated organic matter can be detected at far lower levels and in a wider range of concentrations than TOC, which would provide a better signal-to-noise ratio for detection of injected COM. The detection limit for TOX is approximately 200 times below the concentration measured in chlorinated stream water (Table 3). Thus, the preliminary information indicates chlorination would be a useful, nondestructive method of addressing the problems previously outlined.

In addition to COM, a conservative salt tracer (KCl) will be injected as a slug prior to the natural gradient experiment and in a separate forced gradient experiment.

6.2 DRILLING METHOD

A 3-in. opening will be created with a vibrocore, using a lined well casing providing a 2-in. core. The vibrocore is a relatively nondestructive (<0.3-m disturbance zone), fast-drilling technique. The core will be removed for inspection, and excess sand at the bottom of the hole will be augered out. The multiple-level piezometers (shown in Fig. 6 and described in the following discussion) can be inserted in the outer casing. That casing will then be removed, allowing the surrounding sand to cave in around the smaller piezometer pipes. A concrete pad will be poured around each pipe at the land surface, as required by the state of South Carolina. Since the pad will be above the water table, no intrusion of grout to the flow system during setup is expected.

6.3 WELL CONSTRUCTION

Pumping wells will be constructed of 2-in. PVC pipe. All pumping wells (both injection and withdrawal wells) will be screened over the length of the aquifer (3 to 4 m), capped at the bottom, and equipped with a seal at the top to aid forced injections.

Monitoring wells (shown in Fig. 6) will consist of bundles of 1/4-in. polyethylene tubing, wrapped around a "clover" of four 5/8-in. PVC tubes. The polyethylene tubing (approximately 10 tubes per well) will be used for sampling and terminated with a Nytex screen at different depths in the borehole (approximately 20 cm apart). The PVC tubes are wider in diameter and are used for water level measurement during the injection.

Table 3. Comparison of fractionation of chlorinated and nonchlorinated colloidal organic matter^a

	<u>Nonchlorinated</u>		<u>Chlorinated</u>	
	Repeat 1	Repeat 2	Repeat 1	Repeat 2
Total organic carbon (TOC) (mg/L)	30.5	30.0	27.9	28.8
Hydrophobic (%)	72	73	71	74
Hydrophobic-acid (%)	59	59	54	51
Hydrophobic-neutral (%)	14	15	18	23
Hydrophilic (%)	28	27	29	26
Halogenated organic carbon (TOX) ($\mu\text{g/L}$): detection limit, 5 $\mu\text{g/L}$			948	858
TOC/TOX ^b for hydrophilic			27.7	25.5
TOC/TOX for hydrophobic-acid			32.5	48.4
TOC/TOX for hydrophobic-neutral			42.7	

^aSummary provided by Frank Dunnivant.

^bComparison of TOC/TOX ratio for each component does not indicate strong preferential reaction with any one fraction.

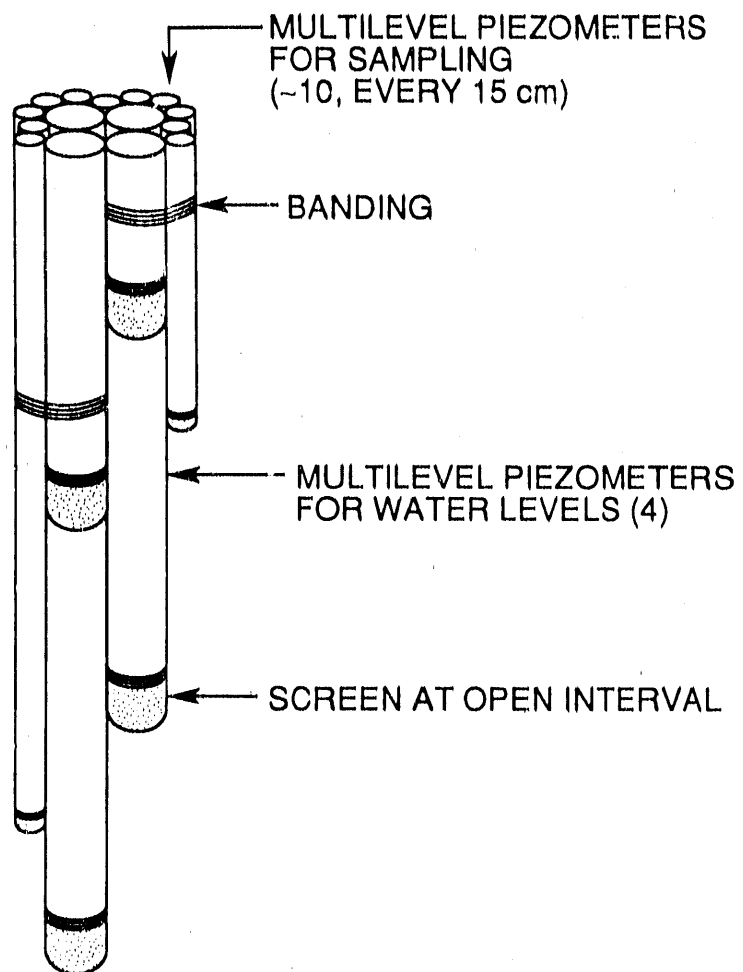


Fig. 6. Well construction diagram showing multilevel piezometer for sampling and water level measurement. Unconsolidated sand collapses around samplers.

6.4 INJECTION AND WITHDRAWAL PUMP

A 220-V centrifugal pump with a side valve to control rates will be used for forced injections (to establish a gradient and to inject water containing COM). Electricity is available at the site.

All of the injection systems are susceptible to clogging, which may be caused by flocculation of colloids and blockage of the well screens. The forced gradient experiments will also provide a test to see if clogging will be a problem. If it is, then laboratory tests to find ways to minimize clogging are needed.

6.5 HOLDING TANK

A reservoir has been constructed near the injection site, made of earthen embankments with two layers of 5-mL plastic as a liner. It will hold 20,000 gal. A roof is constructed over the reservoir, and a screen surrounds the sides to prevent contact by wildlife.

6.6 FIELD SAMPLING FOR COLLOIDS AND OTHER GEOCHEMICAL PARAMETERS

A peristaltic pump at the land surface will be used to collect samples from the piezometers (all depths <25 ft). Colloid samples will be collected in a flow-through system that prevents exposure to atmospheric oxygen during collection (Fig. 7). For example, the sample water enters nitrogen-filled collection bottles through a syringe cap rather than a bottle open to the atmosphere.

After the gradient for each forced gradient experiment has come to hydrologic equilibrium, samples will be collected to measure autochthonous (native) colloids. These analyses can be used to try to find an induced gradient that will minimize transport and interference of natural colloids with injected colloids or to determine the degree of interaction. A sampling rate of 100 mL/min has been suggested.

Other constituents measured to describe the sample include pH, Eh, dissolved oxygen (DO), redox couples, cations, and anions (Table 4). Complete chemical screening will be done for only a few samples. A glove bag will be used to check some redox species in the field with the use of ampules. A flow-through cell will be used for unstable parameters (pH, temperature, DO, Eh).

These additional geochemical parameters will be used to monitor stability of the solutions as the experiments progress and to suggest what chemical and microbiological reactions might need to be considered further (e.g., microbiological activity, changing redox status).

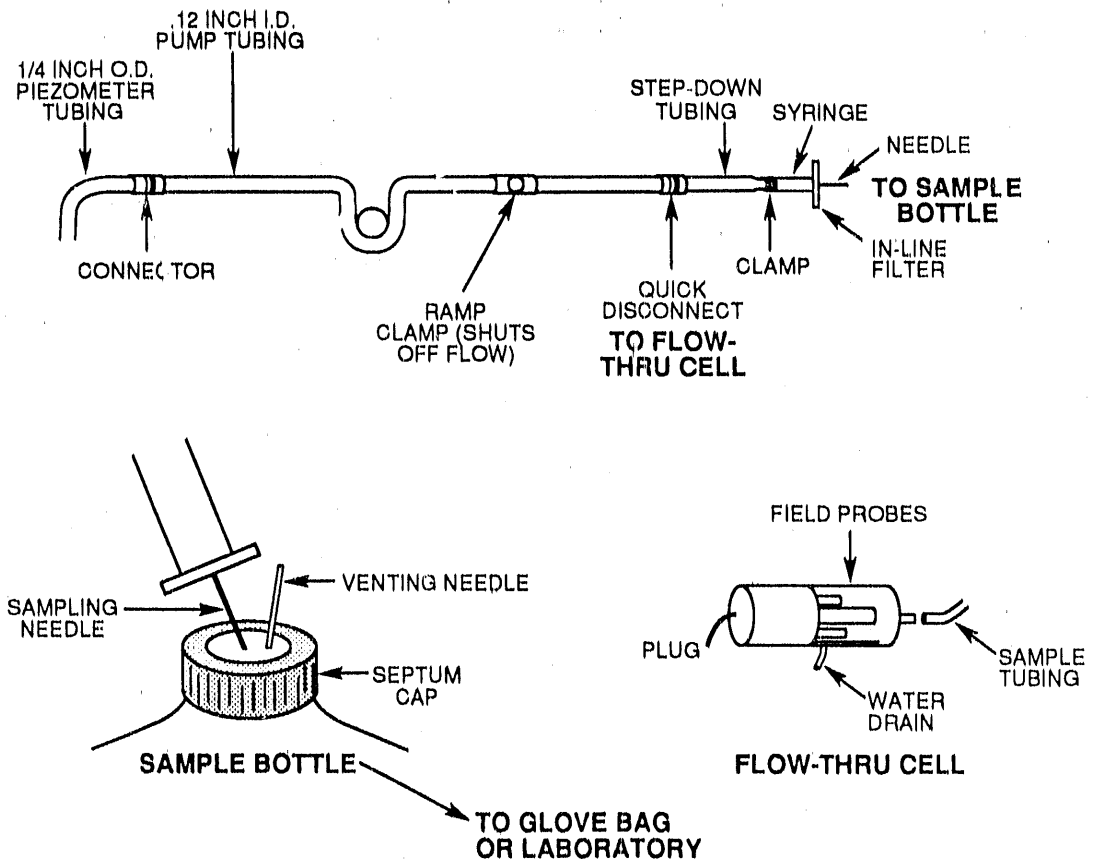


Fig. 7. Sampling system for collection of groundwater samples without atmospheric contact.

Table 4. Proposed Sampling Summary^a

Analyte	Location	Field method
Dissolved organic carbon (DOC)	F, G, and L	S
DOC fractions	L	
Salt tracer	F	P
pH	F, C	P
Dissolved oxygen	F, C	P
Eh	F, C	P
Temperature	F, C	P
Conductivity	F, C	P
Alkalinity	F	T
Total inorganic carbon	L	
Redox couples (Fe, S, N)	F	A
Cations	L	
Anions	L	
Inorganic colloids	L [*]	

^a L = lab, F = field, C = flow-through cell, G = glove bag, L^{*} = possible field measurement with Massachusetts Institute of Technology or Argonne National Laboratory collaboration, P = probe, A = ampule (Chemet kit), S = spectrophotometer, and T = titration.

6.7 SAMPLING SCHEME

The number of samples and sampling interval required for each experiment will be estimated from a one-dimensional advection-dispersion model. A preliminary estimate of dispersion from other field-scale experiments in sandy aquifers indicates 2-h sample intervals would be needed for the conservative tracer at a distance of 2 m from the injection well for the forced gradient experiment with the proposed gradient of 0.1 (Fig. 8). The number of samples in subsequent experiments will depend on field values of dispersion determined during the first experiment.

Longer intervals will be needed for the nonconservative COM, and monitoring for >20 d might be expected around core 4, the first experiment site (Fig. 9). The length of time needed for monitoring depends on the retardation factor for the COM, which has only been estimated in the laboratory. Retention could be stronger in the field if iron oxides provide more binding sites than predicted, or breakthrough could occur sooner if hydrologic factors (e.g., preferential flow paths) dominate transport. Thus, groundwater samples will be monitored for COM at different depths before expected breakthrough.

If no breakthrough of COM is detected, destructive sampling of the injection site to measure COM sorbed on the aquifer material will be used to test hypotheses. Cores will be collected along the transect between the injection and withdrawal well, and the aquifer material will be analyzed to determine the quantity of TOC and TOX sorbed. From these data, the extent of migration of injected COM can be determined, as well as a retention coefficient.

6.8 PHASE I: FORCED GRADIENT EXPERIMENT

6.8.1 Well Array

The well array for the forced gradient experiments is referred to as a doublet test, with one injection well and one withdrawal well (Fig. 10). The monitoring wells would be placed on a line between these two wells, where tracer concentrations should be maximized and flow should be closest to one dimensional. The distance between the withdrawal and injection wells for the first experiment is 5 m. The monitoring wells are located 1.5 m and 3 m from the injection well, where the gradients are fairly uniform. An advantage of having two monitoring wells is to provide a repeat experiment at a slightly later time (further distance). The well spacing was designed to provide a two-order-of-magnitude increase in hydraulic gradient (from 0.001 to 0.1),

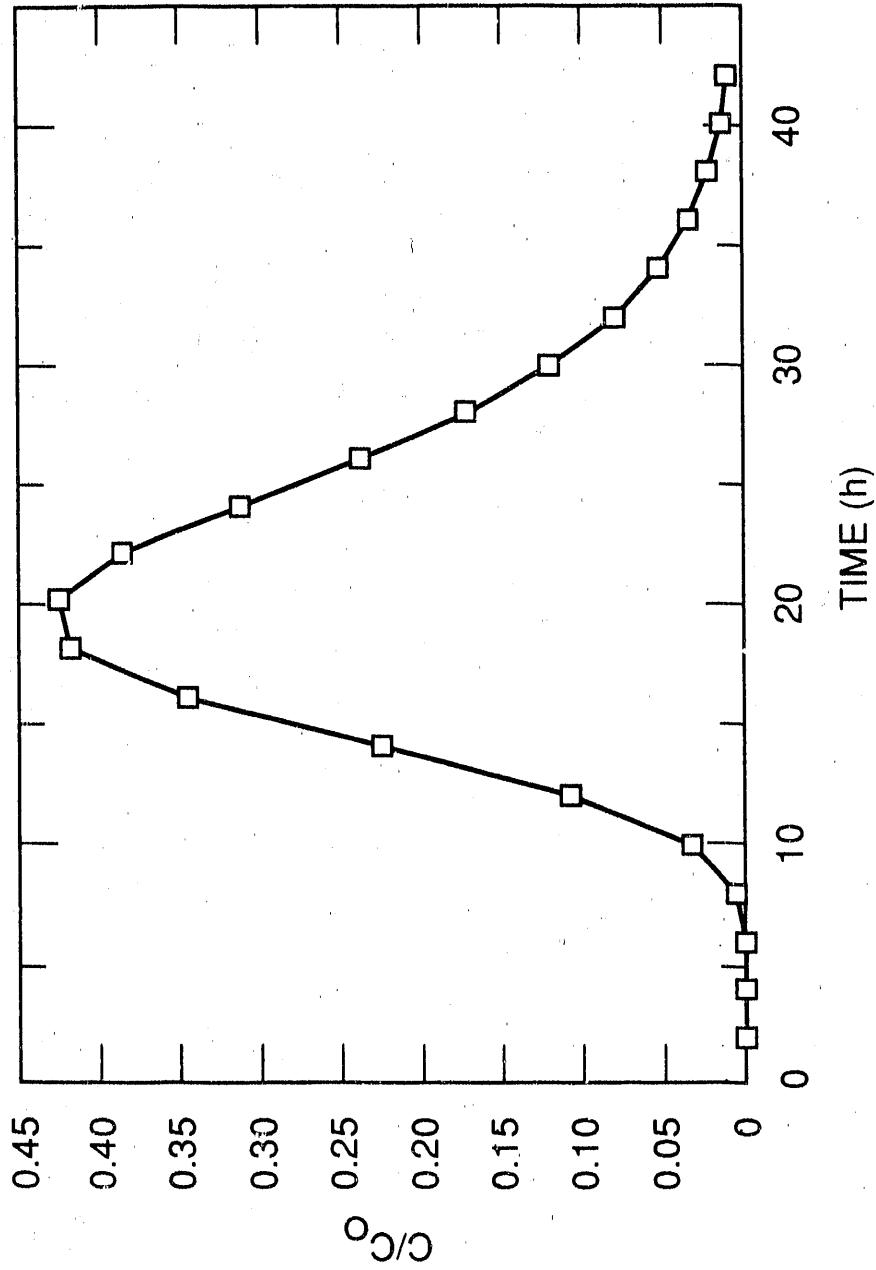


Fig. 8. Modeled Cl breakthrough for first forced gradient experiment, for $v = 10.8$ cm/h, dispersivity = 10 cm, 6000-L slug.

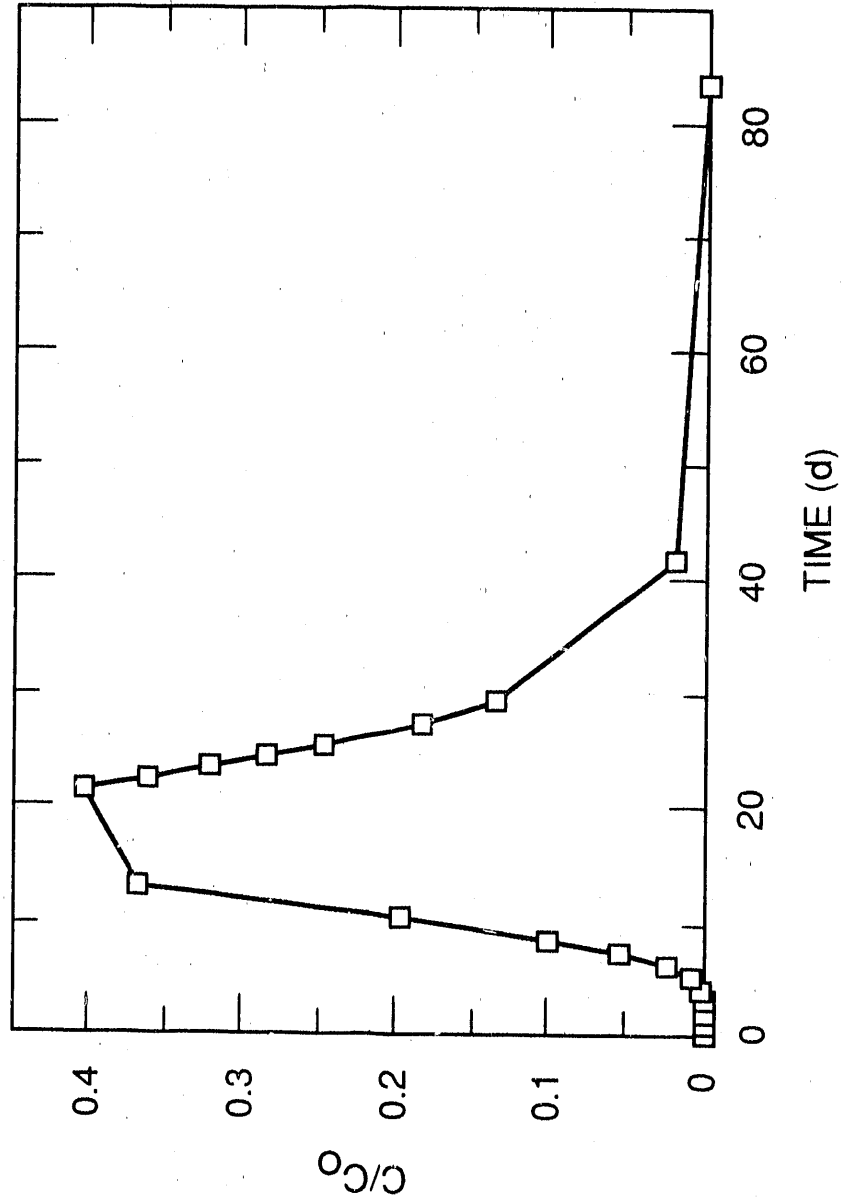
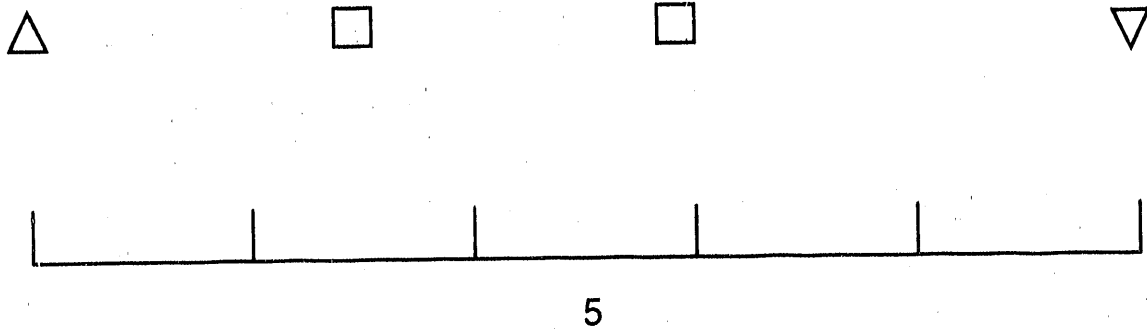


Fig. 9. Modeled colloidal organic matter breakthrough for forced gradient experiment:
 $v = 10.8$ cm/h, dispersivity = 10 cm, $R = 41$, 100,000-L slug.

ORNL-DWG 90M-8929



- △ INJECTION WELL
- ▽ WITHDRAWAL WELL
- MULTILEVEL MONITORING WELL

Fig. 10. Forced gradient well array.

based on estimated hydraulic conductivity at the site and the steady-state Thiem equation (Fig. 11).

6.8.2 Injection Rate

Over the course of a series of forced gradient experiments, different flow rates will be used to determine the effect of flow rate on mobility of existing colloids and injected colloids. The pumping rate determined for the first experiment (based on the Thiem equation as discussed previously) to produce a 0.1 hydraulic gradient is 300 mL/s (~5 gal/min). This pumping rate is toward the upper end of flow rates, limited by dewatering or flooding of the withdrawal and injection wells, respectively. The injection and withdrawal rates will be equal, and withdrawn water will be reinjected in a continuous loop when the COM-rich stream water is not being injected. The actual limits and ranges of flow rates to be tested must await the first field test, when the effects of the actual permeabilities of the aquifer can be measured.

6.8.3 Series of Forced Gradient Experiments

The first stage (Cl^- injection) was conducted in May 1989, and the results are summarized in Appendix B. The forced gradient experiment will proceed in three stages, with experiment conditions and objectives described in Table 5. The first experiment will be a slug injection of the conservative Cl^- tracer. A preliminary conservative tracer experiment was strongly recommended by reviewers of the first draft of this injection plan. The second experiment, in the same set of wells, will be a measure of autochthonous (native) colloids collected at different flow rates induced by forced gradients. The third experiment will be a continuous injection of stream water containing COM (in the same set of wells). The design and location of future experiments will depend on the data and outcome of these first three experiments.

6.9 PHASE II: NATURAL GRADIENT EXPERIMENT

6.9.1 Well Array

The design of the natural gradient experiment (e.g., well spacing) will be modified based on the results of the forced gradient experiments. The initial plan is to use a line of fully penetrating injection wells, six wells ~1 m apart. Multilevel monitoring wells

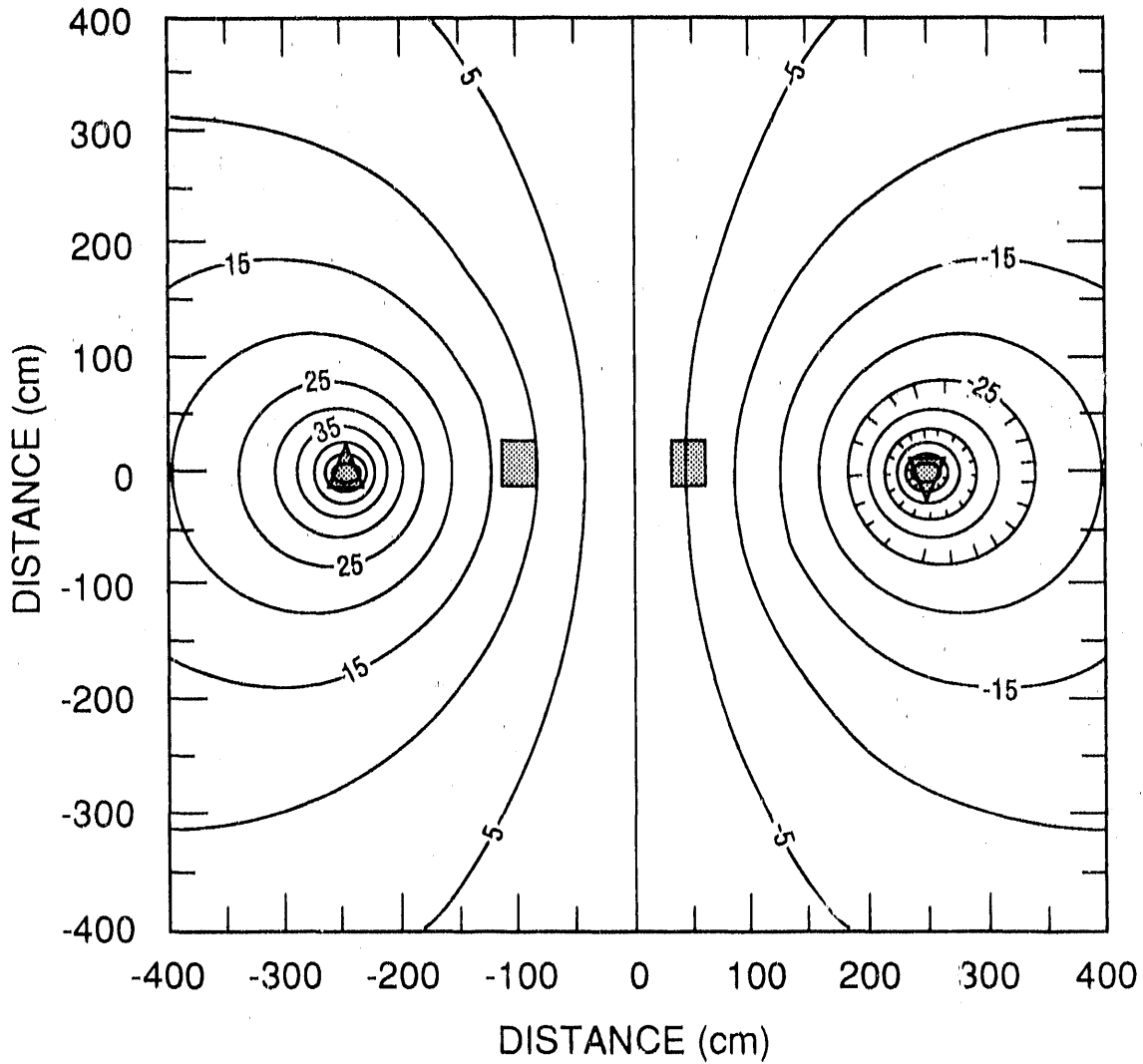


Fig. 11. Forced gradient drawdowns in centimeters predicted by steady-state Thiem equation with 300 mL/s injection and withdrawal rates, 350-cm aquifer thickness, $K = 0.01$ cm/s. Monitoring wells are located at hydraulic gradient of approximately 0.1.

Table 5. List of experiments for first injection well site

Experiment 1: Chloride injection

Conditions: Pumping rate: 100-300 mL/s
~2000-gal slug of KCl solution injected
Sample at 2 m and 3.5 m from injection well
Monitor for Cl every 2 h

Objectives: Determine hydraulic conductivities, dispersion coefficients at field site
Test equipment, sampling techniques, logistical support
Determine reasonable sampling rate
Determine reasonable range of velocities for experiment 2

Experiment 2: Autochthonous colloid mobility under different flow velocities

Conditions: Set up three different pumping rates to create different velocity fields
Collect samples to check for autochthonous colloids

Objectives: Test effect of flow velocities on colloid mobility
Test cascade ultrafilters (if available from Argonne National Laboratory)
Analyze samples with scanning electron microscope

Table 5. List of experiments for first injection well site (con't)

Experiment 3: Colloidal organic matter (COM) stream water injection

Conditions: Pumping rate: 300 mL/s or optimum rate determined from experiments 1 and 2
Inject several thousand gallons of stream water containing COM (up to 8 d of injection)
Monitor at 2 and 3.5 m from injection well
Collect samples every few hours, to be determined by dispersivity measurement (up to 20 or 30 d of monitoring expected)

Objectives: Test colloid mobility hypothesis
Determine variability of retention in different layers and obtain field value for retardation
Determine which fractions of COM are mobile
Determine whether background geochemical conditions (e.g., dissolved oxygen, pH) are stable throughout injections
If necessary, destructively sample aquifer material to better understand retention mechanisms

will be placed 1, 2, 4, 8, and 16 m down gradient from the injection line, with three to five wells in each line.

6.9.2 Injection Rate

The injection rate for the natural gradient experiment will be determined after the forced gradient experiments are complete. It will be necessary to consider several factors in determining the injection rate: (1) desired flow velocity, (2) effects on the water table, (3) effects on well clogging and mobilization of colloids, and (4) dilution of the injected COM.

APPENDIX A: SUMMARY OF INJECTION PLAN REVIEW

A.1 AGENDA FOR MEETING WITH REVIEWERS

AGENDA

South Carolina Colloid Injection Experiment Review

PURPOSE: The purpose of this one-and-a-half-day meeting is to obtain a technical review of proposed plans for an intensely monitored field-scale colloid tracer injection experiment.

THURS., FEB. 23

7:15 - 8:00 Breakfast on your own

8:00 Leave for Baruch Institute (meet in hotel lobby)

I. Presentation and discussion of research program: In this section we will present our research plan for studying colloid mobility. Although there are a number of semiformal presentations, we have allowed time for questions and discussion under each topic. The goal of this section is to present a clear set of tasks for the research and to reach a consensus on the purpose and merit of these tasks.

I.A. Overview of colloid research: We will begin by describing the broad research plan and laboratory research in support of the injection experiment.

9:00 - 9:05 Introduction

9:05 - 9:45 Background on colloid research (McCarthy)
Overview of research tasks
Discussion of hypotheses

9:45 - 10:30 Laboratory research in support of project (Jardine)--
preliminary findings & proposed experiments

10:30 - 10:45 Break

I.B. Discussion of injection site: We will discuss existing data to characterize the site and visit the location of the proposed injection experiment.

10:45 - 11:15 Review of existing field data (Toran & Williams)

11:15 - 12:00 Discuss regulatory environment (Williams)
Discuss proposed injection & monitoring schemes (Toran & Williams)

- 12:00 - 1:00 Lunch catered on site
- 1:00 - 3:00 Visit field site (Williams)
Review field equipment

II. Revisions of the research plan: In this section, we will focus on critiques of the research plan. The goal is to come up with a specific set of revisions that will improve the injection experiment and the overall research.

II.A. Injection plan: We will begin by working on a consensus about the goals and techniques to be used in the field injection experiment. Particular emphasis will be placed on potential logistical, sampling, and characterization problems we may encounter and on suggestions from reviewers concerning how to avoid or deal with these practical problems. The decisions made in this discussion will be used to write the final draft of the injection plan.

- 3:00 - 3:30 Data acquisition, analysis, and expected results
(Toran)
- 3:30 - 5:00 Critique and discussion (group)
Reach a consensus on decisions about injection design
- 5:00 Adjourn for dinner

FRI., FEB. 24 (Meeting in conference room at Best Western, Myrtle Beach)

II.B. New research and modeling needs: We will discuss statistical approaches proposed for the research and discuss other possible research needs. We will reach a consensus about future directions of the research and whether the current plan will lead to those directions.

- 8:30 - 9:15 Discuss geostatistical approaches to spatial and
temporal variability (Jardine)
- 9:15 - 10:00 Reviewers' suggestions for modeling approaches (Toran,
Sudicky, Killey)
- 10:00 - 10:45 Alternative field techniques (Killey, Sudicky)
- 10:45 - 11:30 Identification of additional research (group)
Reach a consensus on future directions
- 11:30 Adjourn for lunch and airplanes

A.2 ATTENDEES AND REVIEWERS

ATTENDEES

Jean Bahr
University of Wisconsin Department
of Geology and Geophysics
Madison, WI 53706

Phil Jardine
Oak Ridge National Laboratory
P. O. Box 2008, MS-6038
Oak Ridge, TN 37831

Doug Killey
Chalk River Laboratory
Environmental Research Branch
Chalk River, Ontario
CANADA K0J 1J0

John McCarthy
Oak Ridge National Laboratory
P. O. Box 2008, MS-6038
Oak Ridge, TN 37831

Bill Penrose
Argonne National Laboratory
ER-203
Argonne, IL 60439

Ed Sudicky University of Waterloo
Department of Earth Sciences
Waterloo, Ontario
CANADA N2L 3G1

Laura Toran
Oak Ridge National Laboratory
P. O. Box 2008, MS-6036
Oak Ridge, TN 37831

Tom Williams
Baruch Forest Science Institute
Clemson University
P. O. Box 596

OTHER REVIEWERS

Dr. Steve Garabedian
U.S. Geological Survey, WRD
150 Causeway St., Suite 1001
Boston, MA 02114

Dr. Warren Wood
U. S. Geological Survey/WRD
MS 431
Reston, VA 22092

Dr. Phillip Gschwend
Department of Civil
Engineering
Massachusetts Institute of
Technology
Cambridge, MA 02139

A.3 SUMMARY OF CHANGES SUGGESTED BY REVIEWERS

1. The reviewers suggested that we would benefit greatly from a tracer on our allochthonous (injected) colloidal organic matter (COM), which would allow us to distinguish it from autochthonous (native) COM in the native aquifer material and groundwater. The tracer suggested is chlorination of the injection water, which would label the injected organic matter with chlorine, as well as kill the bacteria as required by the injection permit. In addition, we might have better detection limits. The chlorination takes place in extreme alkaline conditions, so the chloride injected in the experiment will not chlorinate any natural COM. A laboratory study has begun to find out what the chemical effects of chlorination would be (i.e., how much our injection COM will be altered).
2. A few simple laboratory column experiments with aquifer material and injection COM were recommended to help design the configuration of the injection, sampling, and withdrawal wells. These experiments will also provide site-specific data for preliminary modeling.
3. Our first injection experiment should be a single injection-withdrawal pair, using a conservative tracer alone. An injection rate of 1 to 7 gal/min has been suggested, but additional calculations (using Thiem equation) were recommended as hydraulic conductivity data become available.
4. Hydraulic conductivity should be characterized as extensively as possible. We have obtained additional cores (12) from the field site to do K measurements, as well as chemical characterization of the aquifer material on an extensive spatial scale.
5. We could sample CO₂ gas before and during the injection experiments to study possible bacterial activity. Dissolved oxygen measurements and total inorganic carbon can provide an initial screen for the possibility of microbial activity during injection.
6. The injection water needs to be sampled periodically during the experiment.
7. Options for the monitoring system and coring were discussed. Bundle piezometers and vibracore were recommended.
8. Linearized K_d's should not be used in modeling the COM breakthrough curves determined in the field.

APPENDIX B: RESULTS OF CHLORIDE TRACER TEST

B.1 FIRST STAGE

The first stage of the forced gradient experiment, the chloride tracer test, was conducted May 18-22, 1989, in the southwest portion of Hobcaw Field (Fig. B-1). Two multilevel monitoring wells were installed (15 cm apart) with 11 different sampling depths between 1.05 and 2.55 m. The tubes were bundled around two 1/2-in. PVC pipes and one 2-in. pipe. These three pipes were used for water level measurements (Fig. B-2) at 2.7 m, 2.2 m, and the water table (approximately 0.6 to 0.9 m). The flow gradient was initiated on May 17, 1989, with a 1 gal/min injection/withdrawal rate. The next day 800 gal of a 100-ppm KCl solution was injected. Each monitoring sample port was analyzed for the breakthrough of chlorine tracer with samples collected approximately every 2-4 h (longer at the end of the experiment) for 4 d. About 600 samples total were collected and analyzed in the field. Several groundwater chemical parameters such as dissolved oxygen, conductivity, pH, and Eh were checked three times during the experiment.

The results of this experiment indicated the following:

1. Hydrologic gradients were constant and stabilized quickly (within 1 d) in response to the forced gradient imposed by pumping the withdrawal well and injecting at the same rate into the injection well.
2. Three distinct velocity zones were observed with depth. The velocity of the fastest and slowest zones differed by almost fivefold (Table B-1).
3. Chloride breakthroughs were observed sequentially at the monitoring wells located 1.5 m and 3 m from the injection well, with peak effluent concentrations between 20% and 100% of the influent concentrations (Fig. B-3). Modeling of the breakthrough curves with the classical advection-dispersion equation revealed large heterogeneities in solute dispersion (Table B-1).

These results are important in planning and anticipating results of future experiments. First, we demonstrated that the forced gradient can be induced and gained valuable logistical experience. Secondly, we determined that future samplings can concentrate on three horizons with markedly different flow rates. Sampling and analysis can be concentrated on more intensive characterization of these three horizons, with minimal investment of effort on intermediate zones. Finally, it was apparent that the "fast" horizon was also characterized by high levels of suspended solids in the groundwater, suggesting a correlation between high flow velocities and colloid mobilization. Based on these observations, we anticipate that strong

contrasts will be observed when the colloidal organic matter (COM) solution is injected. We anticipate that chemical interactions of COM with aquifer material will control transport in the "slow" horizon because the slow transport will permit equilibration of the COM with the aquifer material. In contrast, we anticipate that hydrology will dominate COM transport in the "fast" horizon. In this case, we expect COM to be rapidly transported by the rapid groundwater flow and have less time to interact with sorptive surfaces. Furthermore, we expect the COM to break through rapidly as an organomineral complex due to sorption of the COM on mobile clay mineral and iron-oxide particles observed at this horizon.



Fig. B-1. Field site for forced gradient experiment. The injection well is on the right; the withdrawal well, on the left. The return piping is also shown (for water recirculation). The two multilevel monitoring wells are inside the tent.



Fig. B-2. Water level measurement in multilevel monitoring well. Small tubes for water sampling are connected to peristaltic pump.

Table B-1. Dispersion and velocity calculation from
CXTFIT, a least-squares curve-fitting model

ID ^a (D/v, cm)	Modeled velocity	Modeled dispersion (v, cm/h)	Dispersivity (D, cm ² /h)
1.5-1.2	6.5	143	22
-2.1	3.4	195	57
-2.4	3.7	349	25
3 -1.2	3	16	5
-2.4	3.3	69	21

^aID number is distance from injection well in meters followed by a dash and depth of injection well in meters.

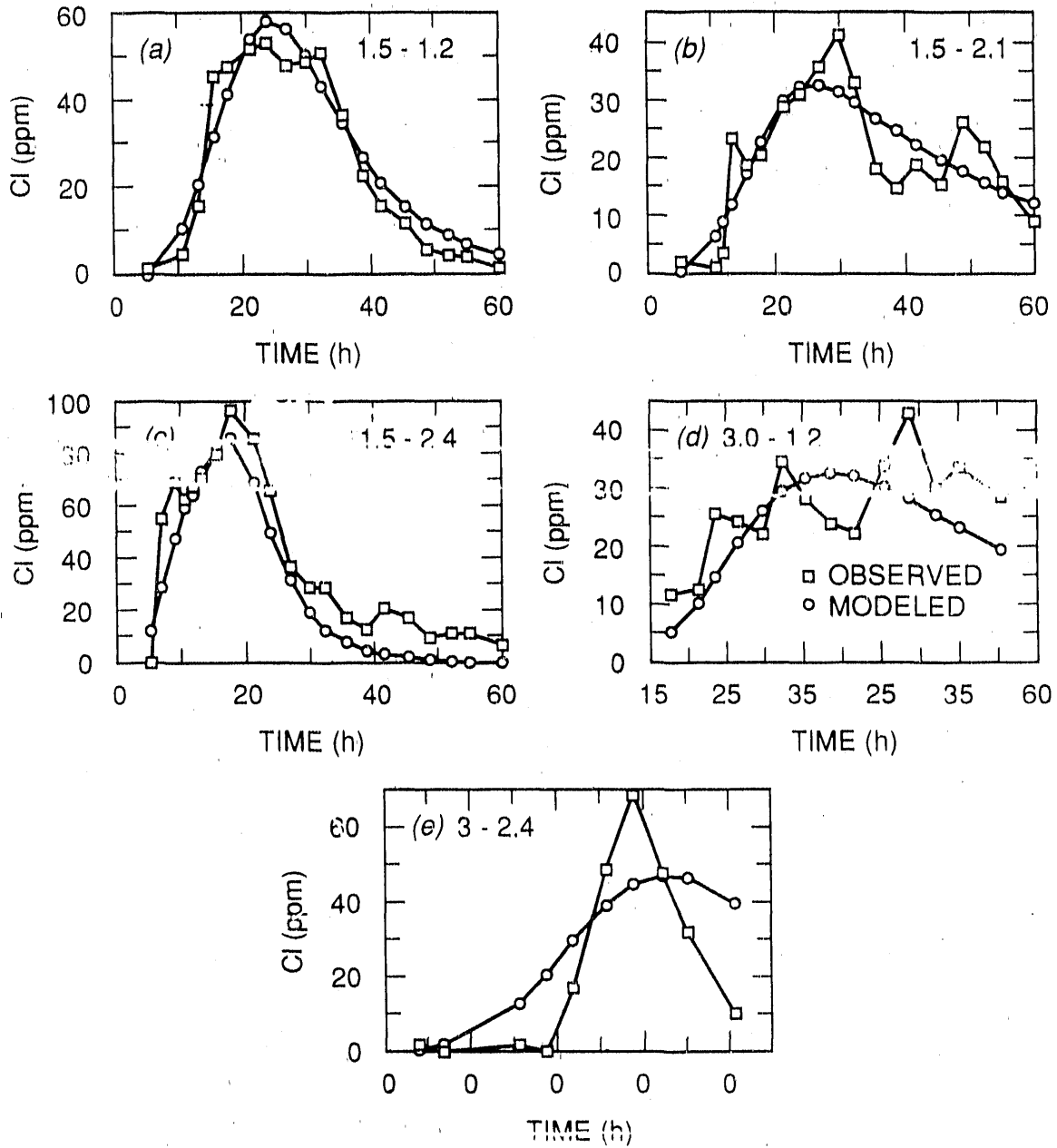


Fig. B-3. Measured and modeled breakthrough curves for Cl injections for IDs (a) 1.5-1.2, (b) 1.5-2.1, (c) 1.5-2.4, (d) 3-1.2, and (e) 3-2.4. ID number is distance from injection well in meters followed by a dash and depth of injection well in meters.

B.2 NEXT STAGES

The next two components of our forced gradient injection plan, the velocity variation and COM injection, were planned for October 1, 1989. Arrangements had been made to have collaborators from Argonne National Lab (ANL) and the U.S. Environmental Protection Agency (EPA-Athens) present during the experiments to analyze groundwater samples by a cascading hollow-fiber filtration apparatus designed by ANL and to characterize mobile particles with respect to abundance, size, and surface charge using photon correlation spectroscopy and particle electrophoresis (using EPA's Zetasizer II). Unfortunately, 1 week before the start of the experiment, Hurricane Hugo devastated the South Carolina coast. The Marine Laboratory at the Baruch Institute was destroyed, the brown-water stream used as a source of COM injection solution was flooded under several feet of saltwater, and Hobcaw Field was submerged by 9 in. of rainwater (but no saltwater intrusion occurred). Furthermore, 30% of the trees in the Baruch Forest Science Institute were blown down, creating logistical problems of site access and power hookups. In addition, the winds appeared to have damaged the reservoir holding the 20,000 gal of injections solution, which leaked from the reservoir. The reservoir is being repaired, and the plastic liner may need to be replaced.

In addition to destroying our source of injection water, the groundwater chemistry of the injection site was affected by the hurricane. The groundwater was anoxic when access to the site was reestablished several weeks after the hurricane. Routine sampling of groundwater chemistry was established to monitor recovery of the site. The reason for the depleted dissolved oxygen concentrations and decreased Eh is not known, but these changes may have been caused by increased biological oxygen demand due to flushing of organic matter or inorganic nutrients from the surface during the flooding. Bacterial activity in the groundwater before Hugo appeared to be low; groundwater from the site did not support growth (increased biomass) of any of three species of bacteria, including a strain isolated from the Hobcaw Field site. Bacterial growth was stimulated if the groundwater was supplemented with inorganic nutrients, especially phosphorus (A. V. Palumbo, ORNL, personal communication to J. F. McCarthy, ORNL, January 1990). Since the dissolved organic carbon (DOC) concentration of the groundwater did not increase substantially after the flooding from the hurricane, it is perhaps more likely that the flooding mobilized inorganic nutrients, which enhanced growth of endogenous bacteria in the aquifer. The forced-gradient DOC injection will have to be delayed until groundwater chemistry is stabilized. Furthermore, it may be necessary to identify another source of COM injection solution since the watershed feeding the stream we had been using has been severely affected by the saltwater. Unless the stream

chemistry recovers soon, this change may require extensive trucking of large quantities of water, possibly from a well-characterized site in North Carolina.

END

DATE FILMED

11 / 21 / 90

