# MOVEMENT AND FATE OF CHLORINATED SOLVENTS IN GROUND WATER: RESEARCH ACTIVITIES AT PICATINNY ARSENAL, NEW JERSEY

By T.V. Fusillo, T.A. Ehlke, and Mary Martin

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## CONVERSION FACTORS

For the use of readers who prefer to use metric (International System) units rather than the inch-pound terms used in this report, the following conversion factors may be used:

| Multiply inch-pound unit | By | To obtain metric unit |
|---|---|---|
| inch (in.) | 25.4 | millimeter (mm) |
| foot (ft) | 0.3048 | meter (m) |
| foot per mile (ft/mi) | 0.1894 | meter per kilometer (m/km) |
| mile (mi) | 1.609 | kilometer (km) |
| gallon (gal) | 3.785 | liter (L) |
| foot squared per day ($ft^2/d$) | 0.0929 | meter squared per day ($m^2/d$) |

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 "Mean Sea Level of 1929".

# MOVEMENT AND FATE OF CHLORINATED SOLVENTS IN GROUND WATER: RESEARCH ACTIVITIES AT PICATINNY ARSENAL, NEW JERSEY

By Thomas V. Fusillo, Theodore A. Ehlke,
and Mary Martin

## ABSTRACT

The U.S. Geological Survey, through its Toxic Waste--Ground-Water Contamination Program, is undertaking an interdisciplinary research study of ground-water contamination by chlorinated solvents and associated contaminants. The purpose of the study is to gain a better understanding of the chemical, physical, and biological processes that affect the movement and fate of these contaminants in ground water. The study is being conducted at Picatinny Arsenal, New Jersey, where metal-plating and metal-etching wastes have contaminated part of the glacial stratified-drift aquifers. This paper describes major areas of research at the site, including: (1) distribution and movement of chlorinated solvents in ground water, (2) behavior of chlorinated solvents in the unsaturated zone, (3) geochemistry of the contaminated ground water, and (4) microbial transformations of chlorinated solvents. This paper also describes objectives and plans of action for these areas of research.

## INTRODUCTION

Ground-water contamination by man-made organic substances is a serious environmental problem in the United States. Studies of ground-water contamination patterns in New Jersey (Page, 1981; Tucker, 1981; Fusillo and others, 1985) and elsewhere (Roberts, 1981; Otson and others, 1982) have shown that volatile organic compounds, in particular volatile chlorinated hydrocarbons, are a major cause of ground-water contamination. The widespread use of these compounds as degreasing agents, dry-cleaning solvents, industrial solvents, septic-system cleaners, and chemical intermediates has resulted in compounds, such as trichloroethylene, tetrachloroethylene, and 1,1,1-trichloroethane being widely distributed in the environment. The chemical and physical properties of these compounds make them fairly mobile in ground water. Detailed information on the chemical, physical, and biological processes that affect their movement is necessary to study the movement and fate of chlorinated solvents in ground water and to evaluate remedial actions.

The U.S. Geological Survey, through the Toxic Waste--Ground-Water Contamination Program, is undertaking an interdisciplinary research study of ground-water contamination by chlorinated solvents and other contaminants related to disposal of wastewater from metal-plating operations at Picatinny Arsenal, New Jersey. The purpose of this study is to improve understanding of the chemical, physical, and biological processes which affect the movement and fate of chlorinated solvents, particularly trichloroethylene, in the subsurface, and to develop predictive models of contaminant transport. This study is one of several on-going interdisciplinary research studies, each of which addresses a different ground-water contamination problem. The other studies presently underway are: creosote contamination in Pensacola, Florida; sewage contamination on Cape Cod, Massachusetts; and crude petroleum contamination near Bemidji, Minnesota, which are described by Franks (1987).

The results of this study are expected to have wide applicability in the evaluation of remedial measures at this site and at the many similar sites throughout the nation. The study will be conducted at Picatinny Arsenal (fig. 1), where the ground water in two areas has been affected by effluent from metal-plating and metal-etching operations. The two areas of ground-water contamination are in the vicinity of buildings 24 and 95, shown in figure 2.

## Purpose and Scope

This report presents an overview of the ground-water contamination that has been documented at the study site, the objectives of the research, and the plan for the research activities at the site. These research activities include the (1) distribution and movement of chlorinated solvents in ground water, (2) behavior of chlorinated solvents in the unsaturated zone, (3) geochemistry of the contaminated ground water, and (4) microbial tranformations of chlorinated solvents.

## Previous Investigations

The U.S. Geological Survey first began studying the ground water at Picatinny Arsenal in 1958. Harold E. Gill and John Vecchioli (U.S. Geological Survey, written commun., 1960) and W.D. Nichols and John Vecchioli (U.S. Geological Survey, written commun., 1965) evaluated the geohydrology and ground-water quality at the Arsenal. In 1982, the U.S. Geological Survey began a study to improve definition of the geohydrologic framework of the valley and determine the extent of ground-water contamination. This investigation included test drilling and the installation of monitoring wells (Harte and others, 1986); application of surface geophysical techniques (Lacombe and others, 1986); and extensive chemical analysis of ground water (Eric F. Vowinkel, U.S. Geological Survey, written commun., 1985; and Sargent and others, 1986).

In addition to work done by the U.S. Geological Survey, the U.S. Army Environmental Hygiene Agency (written commun., 1972 and 1983), and Princeton Aqua Science (written commun., 1981) have documented the operations of the facilities at buildings 24 and 95 and the results of preliminary investigations of ground-water contamination.

## Acknowledgments

The cooperation and assistance of the staff of the U.S. Army Armament Research, Development and Engineering Center at Picatinny Arsenal in the development of this project is greatly appreciated.

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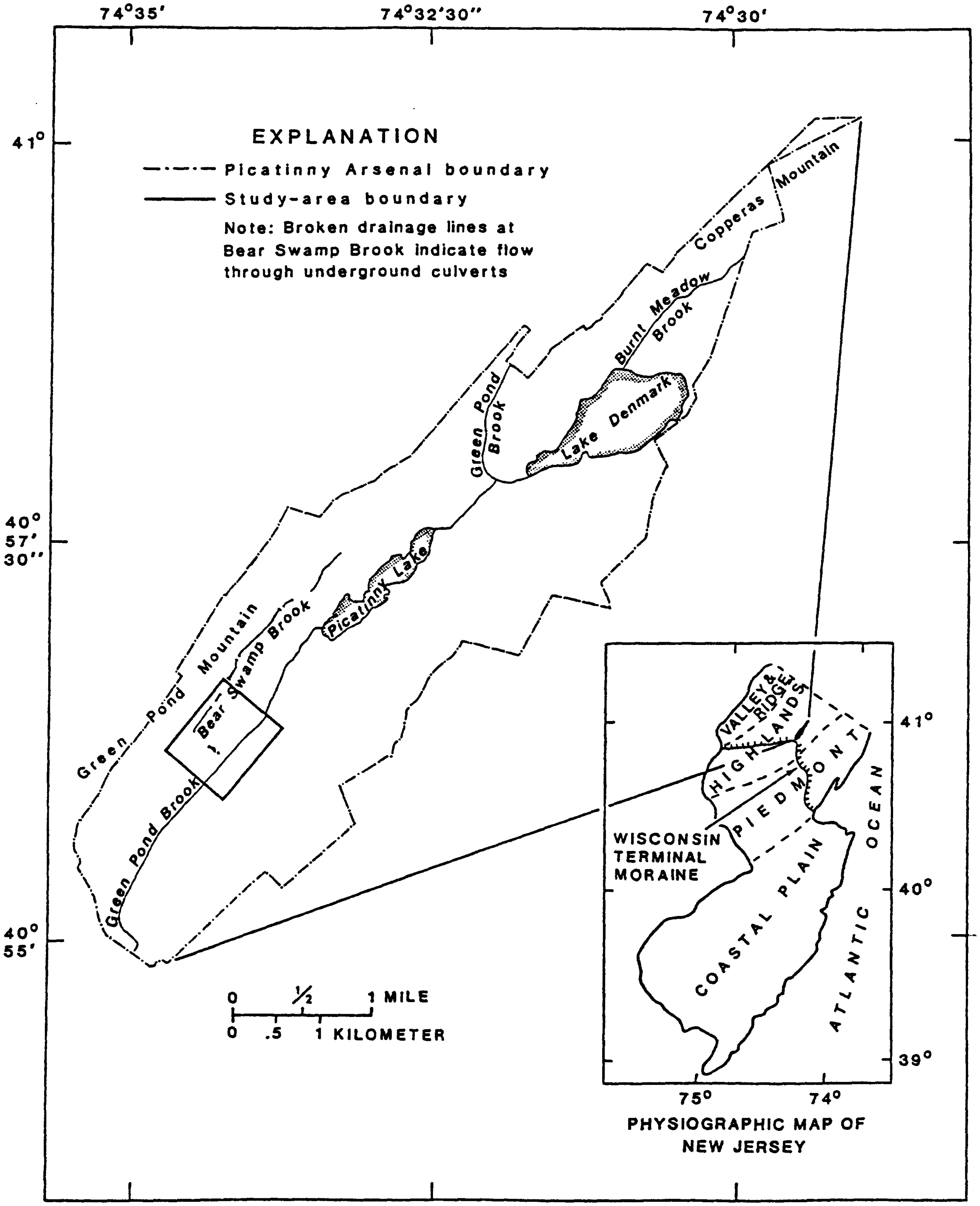

Base from U.S. Geological Survey
1:24 000 topographic quadrangles

Inset map modified from Owens
and Sohl (1969, fig. 3)

Figure 1.--Location of the study area.

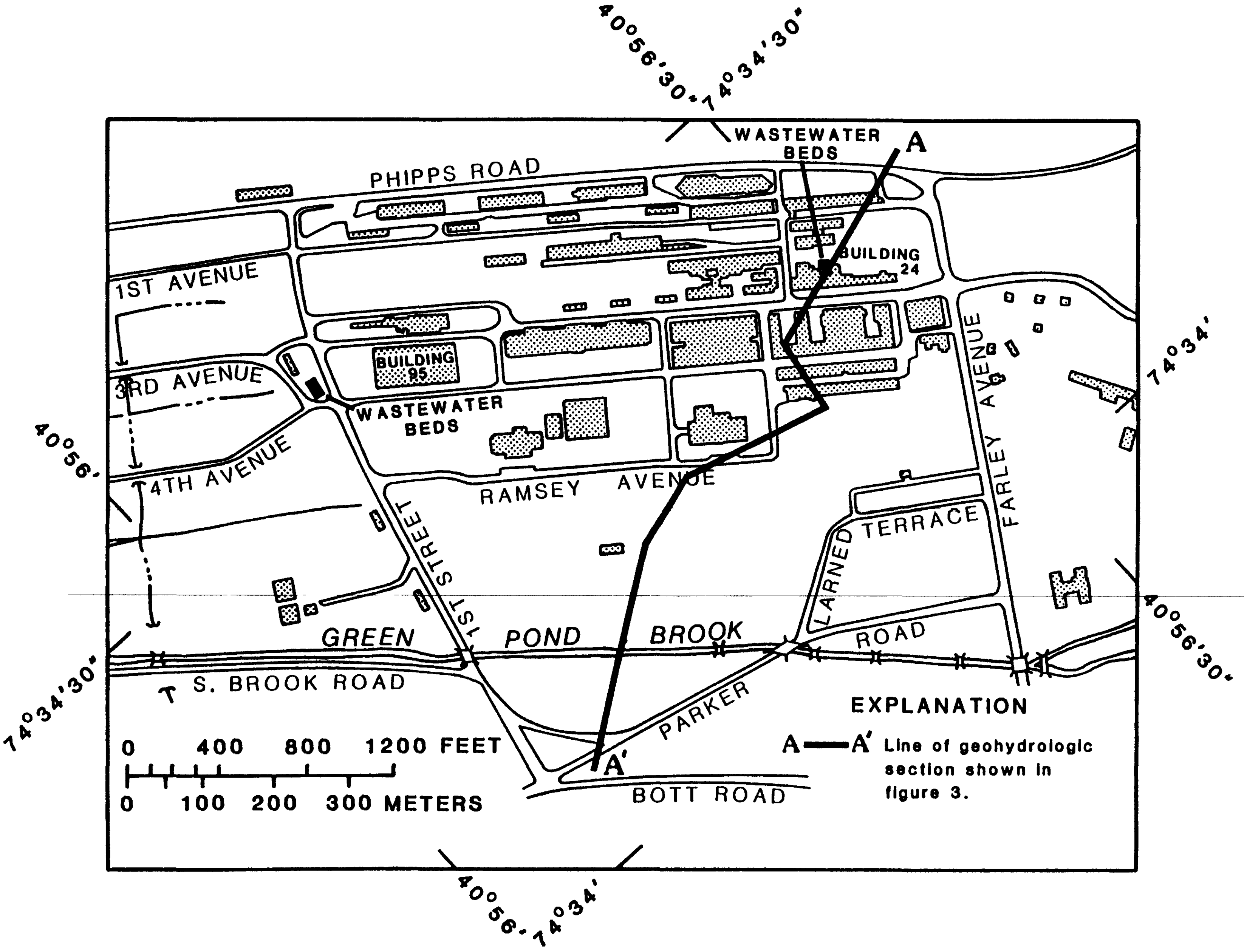

Figure 2.--Location of wastewater disposal beds at buildings 24 and 95.

## DESCRIPTION OF THE STUDY AREA

Picatinny Arsenal is located in north-central New Jersey (fig. 1). The installation, known as the U.S. Army Armament Research, Development, and Engineering Center, employs approximately 6,400 people in research and development of munitions and weapons. The Arsenal covers 6,491 acres and contains about 1,500 buildings serviced by approximately 85 miles of road (Sargent and others, 1986).

The Arsenal has a long history of explosives manufacture that began in the middle 1800's. In 1908, it was designated a U.S. Army Arsenal. During World War II, 20,000 people were employed producing artillery, ammunition, bombs, high explosives, pyrotechnics, and other ordnance items. The Arsenal was a major source of munitions for the Korean Conflict and the Vietnam War.

### Hydrogeologic Setting

Picatinny Arsenal is located in the central part of the New Jersey Highlands (fig. 1)--a region characterized by northeast-to-southwest trending ridges separated by generally deep, narrow valleys. The Arsenal is located in a valley between Green Pond Mountain and an unnamed ridge. Four bedrock units are found at the Arsenal; they are, in ascending order: Precambrian gneiss, the Hardyston Quartzite, the Leithsville Formation, and the Green Pond Conglomerate. The southwestern boundary of the Arsenal is at the edge of the terminal moraine of the Wisconsin glaciation. The valley north of the moraine contains unstratified and stratified drift; thickness of the drift is about 80 feet near Picatinny Lake and greater than 200 feet at the southwestern boundary.

A generalized hydrogeologic section across the valley in the vicinity of the contaminant plume at building 24 (fig. 3) shows an unconfined stratified-drift aquifer approximately 35 feet thick; a confining unit of variable thickness; and a confined stratified-drift aquifer, ranging from 20 to 75 feet in thickness, overlying a bedrock aquifer. The unconfined aquifer is composed of unconsolidated sediments ranging from gravel and coarse sand to fine clay and is continuous throughout most of the study area (Harte and others, 1986). A map of the water table is shown in figure 4. The depth to water in the vicinity of the contaminant plume ranges from about 5 to 15 feet. The hydraulic gradient in the unconfined aquifer ranged from about 0.0025 [13 ft/mi (feet per mile)] to 0.0053 (28 ft/mi) during 1984 in the area of building 24 and averaged about 0.0025 (13 ft/mi) with little variation in the area of building 95. The average horizontal hydraulic conductivity of the aquifer is estimated to be 60 ft/d (feet per day) in the area of building 24 and 20 ft/d in the area of building 95. Average ground-water flow rates are estimated to be 1 ft/d in the area of building 24 and 0.1 ft/d in the area of building 95 (Eric F. Vowinkel, U.S. Geological Survey, written commun., 1986).

The confining unit that separates the unconfined aquifer from the confined stratified-drift aquifer is composed of interbedded fine sand, silt, and clay. This confining unit is probably not continuous across the valley and is leaky. Vertical hydraulic conductivity of the confining unit is estimated at 0.6 ft/d.

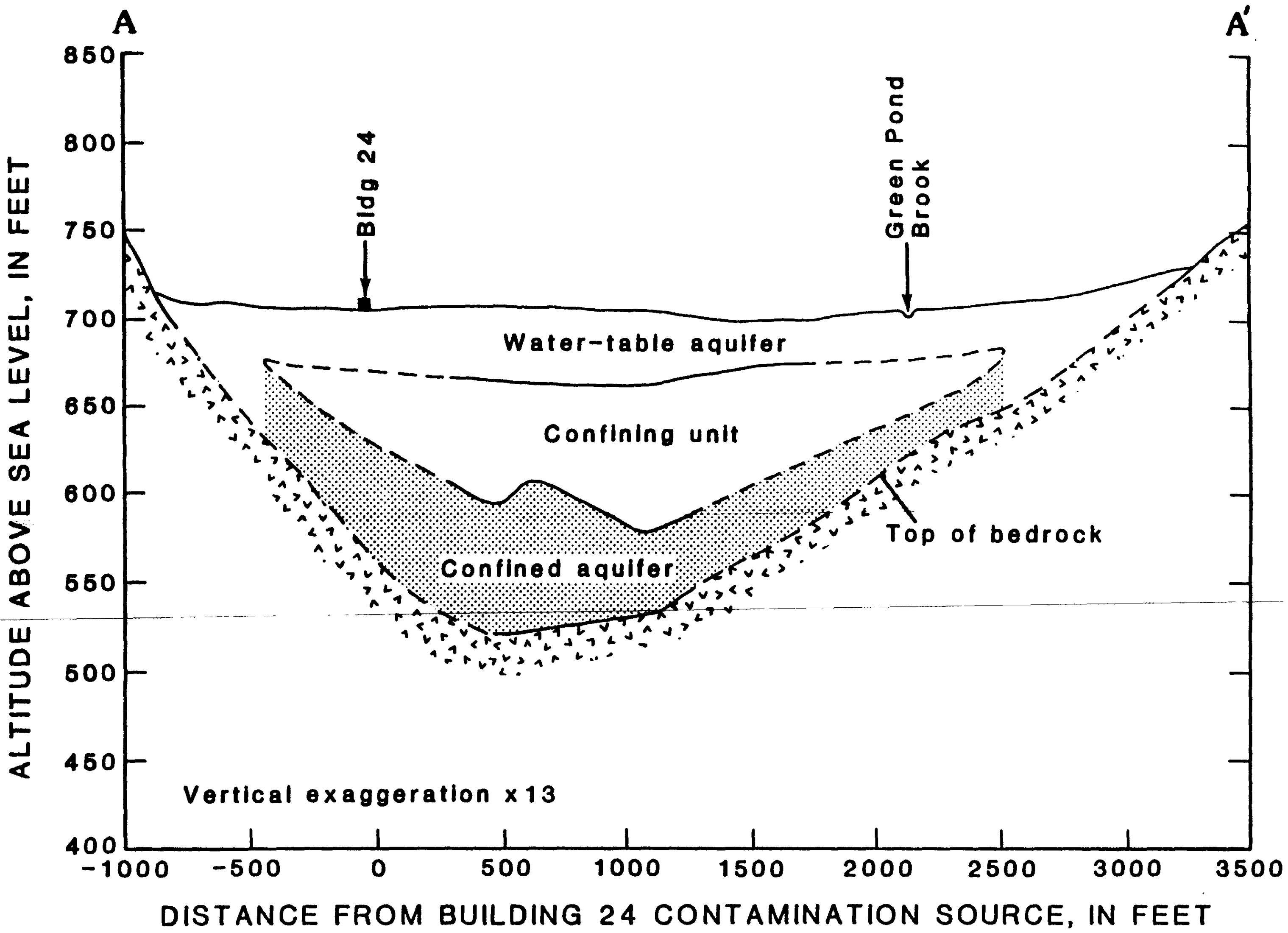

Figure 3.--Generalized geohydrologic section.

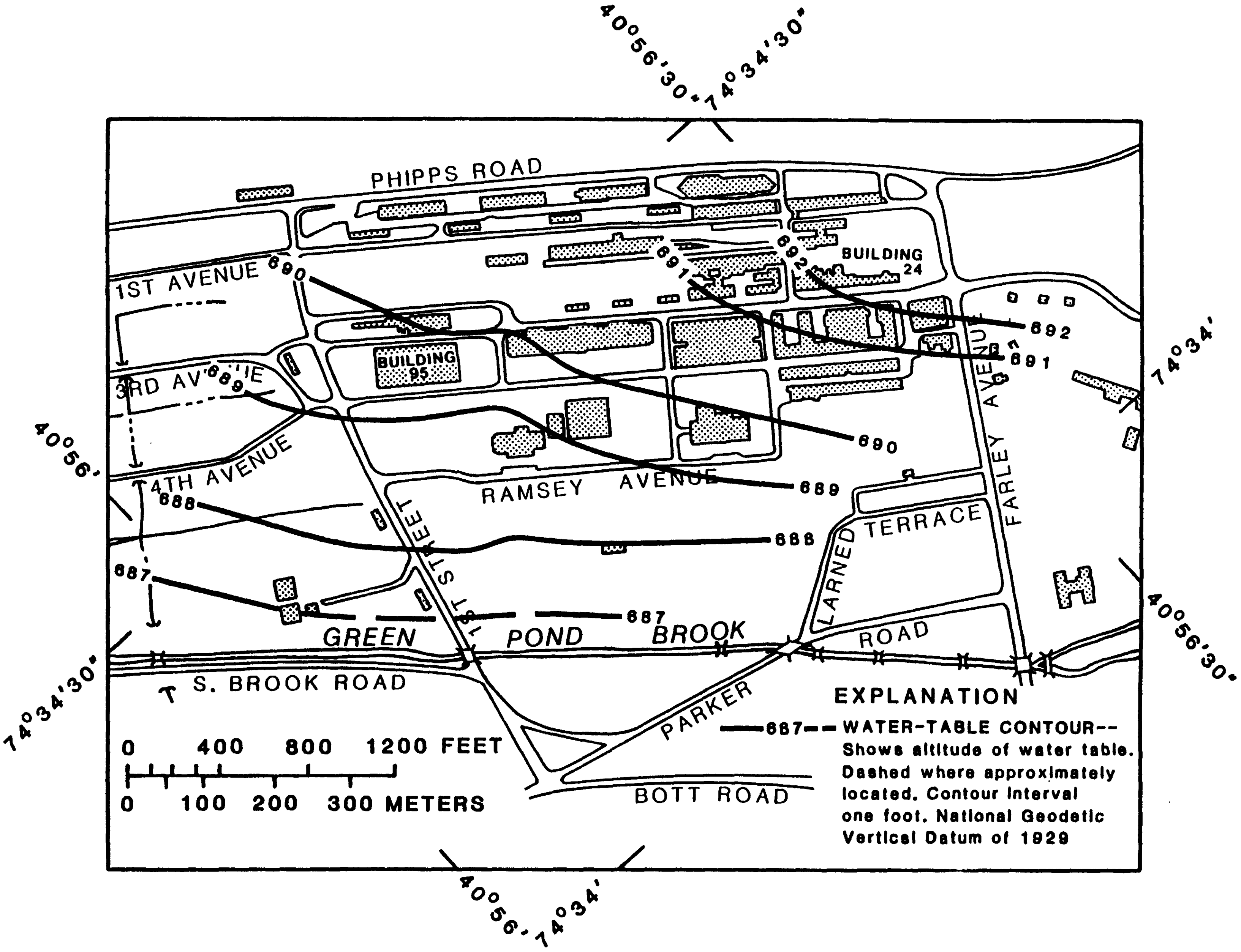

Figure 4.--Altitude of water table, August 1985.

The confined stratified-drift aquifer is composed of predominately coarse sands, with some gravel, pebbles, cobbles, and boulders (Harte and others, 1986). The transmissivity of the confined aquifer in the area of building 24 is estimated at 7,500 $ft^2/d$ (feet squared per day) (Mary Hill, U.S. Geological Survey, written commun., 1984). Two supply wells are screened in this aquifer in the study area. These wells were used for potable water supply until they were found to be contaminated with chlorinated solvents in 1981. Withdrawals from these wells have affected the movement of contaminants in the ground-water system.

Bedrock in the study area consists mainly of dolomite of the Leithsville Formation. It is separated from the overlying confined stratified-drift aquifer by a zone of weathered bedrock.

## Ground-water Contamination

### Building 24 Area

From 1960 to 1981, wastewater was discharged from a metal-plating operation in building 24 into two unlined filtration pits, which flowed into two sets of concrete settling tanks, and then discharged into Bear Swamp Brook, a tributary to Green Pond Brook. During 1979, wastewater discharge was approximately 10,000 gal/d (gallons per day), with a maximum daily discharge of 21,600 gallons (Michael Ruiz, U.S. Army, oral commun., 1985). The resulting infiltration of wastewater into the ground-water system produced a plume of contamination in the water-table aquifer, which emanates from the building 24 area and follows the general water-table gradient. The most significant contamination is limited to the water-table aquifer; however, because of seepage around or through the confining unit, trichloroethylene has been detected in some wells in the confined aquifer.

The largest organic component of the contaminant plume is trichloroethylene, with concentrations ranging from 25,000 μg/L (micrograms per liter) adjacent to the lagoons to near detection limits at a distance of about 1,500 feet from the lagoons. The generalized distribution of trichloroethylene in the unconfined aquifer is shown in figure 5. In addition to trichloroethylene, other organic compounds have been detected; maximum levels were 197 μg/L for tetrachloroethylene, 165 μg/L for 1,1,1 trichloroethane, and 542 μg/L for 1,2 trans-dichloroethylene. Since 1981, elevated levels of several inorganic constituents have been detected; maximum levels were 61 μg/L for cadmium, 150 μg/L for chromium, 97 μg/L for lead, 20 μg/L for selenium, 430 μg/L for cyanide, and 409 μg/L for copper. Recent data, however, show that concentrations of most inorganic constituents have decreased significantly from these maximum levels.

### Building 95 Area

Prior to May 1981, wastewater from a metal-plating and etching operation in building 95 was discharged into two unlined sand filtration beds; sludge from the treatment process also was placed into an adjacent sludge drying bed. Drain lines discharged most of the effluent from these beds to a nearby drainage ditch. Some of the effluent, however, infiltrated into the ground-water system. In 1981, the filtration beds and sludge

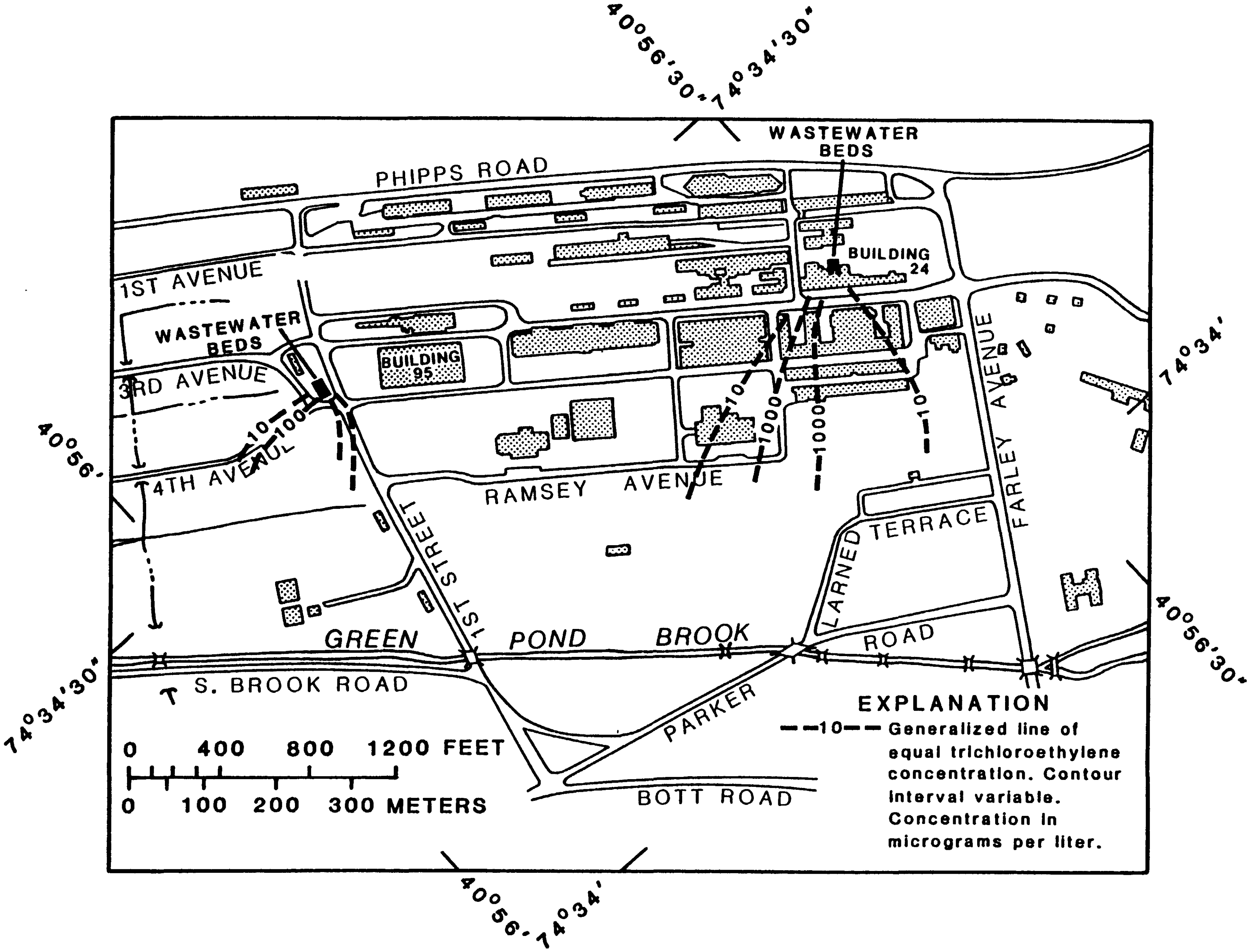

Figure 5.--Generalized distribution of trichloroethylene in the unconfined stratified-drift aquifer in the area of buildings 24 and 95, August 1985.

drying bed were excavated and replaced with clean fill. Contaminants in the wastewater from the building 95 operation included 1,1,1-trichloroethane, chromium, and other metals from the plating process, sulfuric acid, hydrochloric acid, and sodium hydroxide.

Because only five observation wells were installed at this site initially, fewer data are available on the composition and extent of ground-water contamination at building 95, as compared to building 24. Chemical analyses of samples from these five wells show contamination; maximum concentrations were 180 μg/L for chromium, 470 μg/L for copper, 23 μg/L for cadmium, 64 μg/L for lead, 50 μg/L for cyanide, 128 μg/L for trichloroethylene, 386 μg/L for tetrachloroethylene, 1700 μg/L for 1,1,1-trichloroethane, and 319 μg/L for 1,1-dichloroethylene. Detailed definition of the areal extent of the contamination is not possible based upon the existing data. Additional wells have been installed and sampled; upon completion of the analyses of these samples, a preliminary evaluation of the areal extent of contamination will be possible.

## RESEARCH ACTIVITIES

Four major areas of research at Picatinny Arsenal have been defined:

1. Distribution and movement of chlorinated solvents in ground water.
2. Chlorinated solvents in the unsaturated zone.
3. Geochemistry of contaminated ground water.
4. Microbial transformations of chlorinated solvents.

Each of these research topics will be discussed in the following sections. Detailed work plans and research hypotheses to be tested, which are not presented here, will be developed in conjunction with the various researchers involved. The relative emphasis placed on each area of research is related to the scientific merits, availability of research personnel, and project funding.

### Distribution and Movement of Chlorinated Solvents in Ground Water

#### Objectives

1. Define the distribution of contaminants in the ground-water system.

2. Determine the physical processes that control the movement of contaminants.

3. Integrate physical, chemical, and biological processes, using simulation models of solute transport to test hypotheses.

#### Approach

A detailed analysis of contaminant distribution and movement in the saturated zone will be done. At present, only limited information is available concerning the vertical variations in contaminant concentrations. Because trichloroethylene and other chlorinated solvents are significantly denser and less viscous than water, the effects of density and viscosity on the distribution of the contaminants must be considered. Determination of the vertical distribution of contaminants will help identify the role of the physical properties of the contaminants in the transport of these compounds.

The determination of the vertical distribution and movement of contaminants will require the collection of additional data. Several nests of small-diameter monitoring wells will be installed in the study area. Upon completion of installation, samples will be collected for analysis of chlorinated solvents, trace metals, and other constituents of interest. Periodic resampling will be performed on selected wells to determine changes in ground-water quality over time.

During the drilling of observation wells, samples of aquifer and confining unit material will be collected. Samples will be analyzed for sorbed organic compounds. Additional laboratory analyses of the samples may include particle-size analyses, porosity, permeability, organic-matter content, clay mineralogy, and content of selected elements.

A considerable amount of information has been collected on the geohydrology of the area. Additional geohydrologic data will be collected during well drilling; these data are expected to improve the definition of the geohydrology at a finer scale. Aquifer tests may be performed after a review of the available hydrogeologic data.

Existing hydrogeologic data were used to develop a preliminary three-dimensional flow model for the area, including the two contamination sites being studied. This model simulated flow in the three aquifers: the unconfined stratified-drift aquifer, the confined stratified-drift aquifer, and the bedrock aquifer. Initial calibration of this model has refined initial estimates of the hydraulic characteristics in the area and the initial approximations to the local boundary conditions.

A more detailed three-dimensional flow model is being developed to better define flow conditions at the two contamination sites. This model will incorporate additional hydrogeologic data collected at the sites and will more closely approximate the natural hydrologic-boundary conditions. The model will be calibrated to water-level fluctuations caused by seasonal changes in recharge, changes in withdrawals, and aquifer-test withdrawals. The flow system defined by this model will be used to develop several smaller-scale solute-transport models. These models will be used to define the movement of conservative constituents. The conservative constituents will be determined by evaluating the results of chemical analyses for inorganic and organic constituents. The solute-transport models will have the same geohydrologic framework as the larger-scale flow model and will have specified flows, calculated from the three-dimensional flow simulations, as lateral-boundary conditions.

Estimates of dispersivity will be determined by model calibration, in which initial estimates of dipersivity are refined until the observed distribution is closely simulated. The results of the detailed investigation of dispersivity in the glacial aquifer at Cape Cod will be evaluated and applied as appropriate. The approach to be used in modeling solute transport will be determined following the definition of the three-dimensional distribution of contaminants in the aquifer and the three-dimensional flow system.

## Chlorinated Solvents in the Unsaturated Zone

### Objectives

1. Determine the vertical distribution of contaminants and major gases in the unsaturated zone, particularly in the vicinity of the contamination source.

2. Investigate the factors that control the partitioning of contaminants between the soil gas, soil particles, and soil water.

3. Investigate the transfer of contaminants between ground water and soil vapor and water in the unsaturated zone.

4. Investigate the application of induced air venting for integrated monitoring of soil gases and for removing contaminants from the unsaturated zone.

### Approach

The unsaturated zone plays an important role in the movement and fate of chlorinated solvents in the subsurface because of the highly volatile nature of these compounds. Volatilization from the upper part of the water table into the unsaturated zone, and from soil moisture and soil particles in the unsaturated zone to the atmosphere, may result in losses of chlorinated solvents from the subsurface system. Sorption onto soil surfaces, chemical partitioning into soil organic matter, biodegradation, and/or chemical degradation also may reduce the concentrations of infiltrating contaminants before they reach the water table. However, contaminants sorbed onto sediments may act as a reservoir of chlorinated solvents that may be released to the ground water during percolation of recharge water or during periods of high water table.

The study of chlorinated solvents in the unsaturated zone will involve the collection of soil samples and soil gas samples for chemical analyses. Soil samples will be collected from land surface to the top of the water table; depth to water ranges from 5 to 15 feet in most of the study area. Samples at selected depths will be analyzed for organic compounds. Other analyses will include particle-size distribution, organic-carbon composition, water content, and clay mineralogy of selected soil samples. At each site, contaminant levels in ground water will be determined by collecting ground-water samples from near the top of the water table. Samples of uncontaminated soil will be collected for use in laboratory experiments to determine the sorption properties of the soil and the role of organic carbon and moisture content in controlling sorption.

Vapor probes will be installed at vertically spaced intervals in the unsaturated zone at each location to enable the collection of samples of soil gases. Periodic collection of soil-gas samples from these probes for analysis of major gases, including oxygen, hydrogen, carbon dioxide, nitrogen, and methane, as well as volatile organic compounds, will provide detailed field data on the distribution of these substances in the unsaturated zone. The installation of air-withdrawal wells in the unsaturated zone will be considered as a method for integrating the monitoring of the unsaturated zone over a larger area than is possible using vapor probes and, also, as a possible method for removal of chlorinated solvents from the unsaturated zone.

## Geochemistry of Contaminated Ground Water

### Objectives

1. Determine in detail the chemical composition of the contaminated ground water.

2. Investigate the chemical processes affecting the movement of contaminants within the aquifer, including sorption/desorption, partitioning, volatilization, ion exchange, dissolution/precipitation, and oxidation/reduction.

3. Investigate the interactions between contaminants and the aquifer matrix, and the role of surface coatings.

### Approach

Purge-and-trap gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS), liquid extraction GC/MS, and atomic-absorption spectrophotometry will be used to analyze water and geologic samples to obtain detailed information on the chemical composition of contaminants in the ground-water system. Data on semivolatile and nonvolatile organic compounds in ground water will be particularly useful in defining the chemical composition of the contamination, because few data on these compounds in ground water at the site are available.

Samples of aquifer and confining-unit sediments will be analyzed by x-ray diffraction to determine the mineralogic composition of the sediments and by x-ray fluorescence to determine elemental composition. Samples from various points in the contaminant plume will be examined to determine the chemical processes affecting contaminant movement and to identify reaction sequences occurring throughout the length of the contaminant plume. Laboratory experiments, such as column studies, may be used to simulate processes occurring in the field. Equilibrium models may be used to test hypotheses about reactions occurring in the contaminant plume. The approach and methods to be used in studying the sediment coatings have not yet been defined; however, it is anticipated that the effects of the surface coatings on contaminant movement and chemical reactions is significant and will be an important part of the study.

## Microbial Transformations of Chlorinated Solvents

### Objectives

1. Characterize the physical, chemical, and biological conditions in the ground water.

2. Investigate the role of bacteria in the transport and fate of the ground-water contaminants.

3. Investigate the effect of the ground-water environment on the rate of specific biotransformations and the relations among the rate of dechlorination of chlorinated solvents and other biotransformation processes, such as methanogenesis, sulfate reduction, and denitrification.

4. Evaluate methods of enhancing the biotransformation process and the potential for the use of biotransformation processes as part of a remedial measure.

## Approach

The detection of organic compounds, such as vinyl chloride and 1,2-cis-dichloroethylene, in several wells at the study site suggests the probable microbial degradation of chlorinated solvents in the ground-water system. These compounds have been detected in previous studies of the dehalogenation of chlorinated ethenes (Lage and Parsons, 1985; Lage and others, 1986).

Water samples from selected sampling points in the area of contaminated ground water will be collected and analyzed for compounds that may be indicators of microbial activity; these compounds include vinyl chloride and 1,2-cis-dichloroethylene. In addition, samples will be analyzed for major ions; nutrients; and dissolved gases, including oxygen, carbon dioxide, nitrogen, hydrogen, and methane. Measurements of pH, specific conductance, temperature, and Eh also will be made. This data will help characterize the subsurface environment as it relates to microbial activity. Measurements of microbial biomass will be made using methods such as the Acridine Orange direct count and the agar spread plate count.

In areas of the aquifer where significant microbial activity is believed to be occurring based on the results of analyses, samples of ground water and aquifer materials will be collected to study the role of microbes in the observed transformation of chlorinated solvents. Initially, laboratory studies will use soil and water microcosms to simulate biodegradation in the saturated and unsaturated zones. The use of radiolabelled trichloroethylene, variations in oxygen tension, and the addition of nutrient and carbon amendments to the microcosms will enable the study of the role of biotransformation in the degradation of these compounds and the effects of environmental conditions on the rate of biotransformation. Of particular interest are the relations among the biotransformation of chlorinated solvents and other biotransformation processes, such as sulfate reduction, denitrification, and methanogenesis.

The results of the field investigation and the laboratory microcosm experiments will be evaluated to determine if biological processes may have a role in the remediation of ground-water contamination at the site, and if chemical amendments to the ground water, such as addition of oxygen or nutrients can enhance this role. Soil-column studies, including procedures to stimulate bacterial growth and varying soil-gas conditions, could be performed as a demonstration clean-up process.

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