



In cooperation with the
U.S. Army Garrison, Aberdeen Proving Ground
Environmental Conservation and Restoration Division
Aberdeen Proving Ground, Maryland

Simulation of Ground-Water Flow and Transport of Chlorinated Hydrocarbons at Graces Quarters, Aberdeen Proving Ground, Maryland

Water-Resources Investigations Report 01-4106

**U.S. Department of the Interior
U.S. Geological Survey**

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by Frederick J. Tenbus and William B. Fleck

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2001

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For additional information contact:

District Chief
U.S. Geological Survey
8987 Yellow Brick Road
Baltimore, MD 21237

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Conversion Factors and Vertical Datum

	Multiply	By	To obtain
	inch (in.)	2.54	centimeter
	foot (ft)	0.3048	meter
	acre	4,047	square meter
	acre	0.4047	hectare
	gallon per minute (gal/min)	0.06309	liter per second
	inch per year (in/yr)	25.4	millimeter per year
	pound, avoirdupois (lb)	0.4536	kilogram

Temperature in degrees Fahrenheit (°F) can be converted to degrees Celsius (°C) by using the following equation:

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32) / 1.8$$

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

Simulation of Ground-Water Flow and Transport of Chlorinated Hydrocarbons at Graces Quarters, Aberdeen Proving Ground, Maryland

By Frederick J. Tenbus and William B. Fleck

Abstract

Military activity at Graces Quarters, a former open-air chemical-agent facility at Aberdeen Proving Ground, Maryland, has resulted in ground-water contamination by chlorinated hydrocarbons. As part of a ground-water remediation feasibility study, a three-dimensional model was constructed to simulate transport of four chlorinated hydrocarbons (1,1,2,2-tetrachloroethane, trichloroethene, carbon tetrachloride, and chloroform) that are components of a contaminant plume in the surficial and middle aquifers underlying the east-central part of Graces Quarters. The model was calibrated to steady-state hydraulic head at 58 observation wells and to the concentration of 1,1,2,2-tetrachloroethane in 58 observation wells and 101 direct-push probe samples from the mid-1990s. Simulations using the same basic model with minor adjustments were then run for each of the other plume constituents. The error statistics between the simulated and measured concentrations of each of the constituents compared favorably to the error statistics of the 1,1,2,2-tetrachloroethane calibration. Model simulations were used in conjunction with contaminant concentration data to examine the sources and degradation of the plume constituents. It was determined from this that mixed contaminant sources with no ambient degradation was the best approach for simulating multi-species solute transport at the site. Forward simulations were run to show potential solute transport 30 years and 100 years into the future with and without source removal. Although forward simulations are subject to uncertainty, they can be useful for illustrating various aspects of the conceptual model and its implementation. The forward simulation with no source removal indicates that contaminants would spread throughout various parts of the surficial and middle aquifers, with the 100-year simulation showing potential discharge areas in either the marshes at the end of the Graces Quarters peninsula or just offshore in the estuaries. The simulation with source removal indicates that if the modeling assumptions are reasonable and ground-water cleanup within 30 years is important, source removal alone is not a sufficient remedy, and cleanup might not even occur within 100 years.

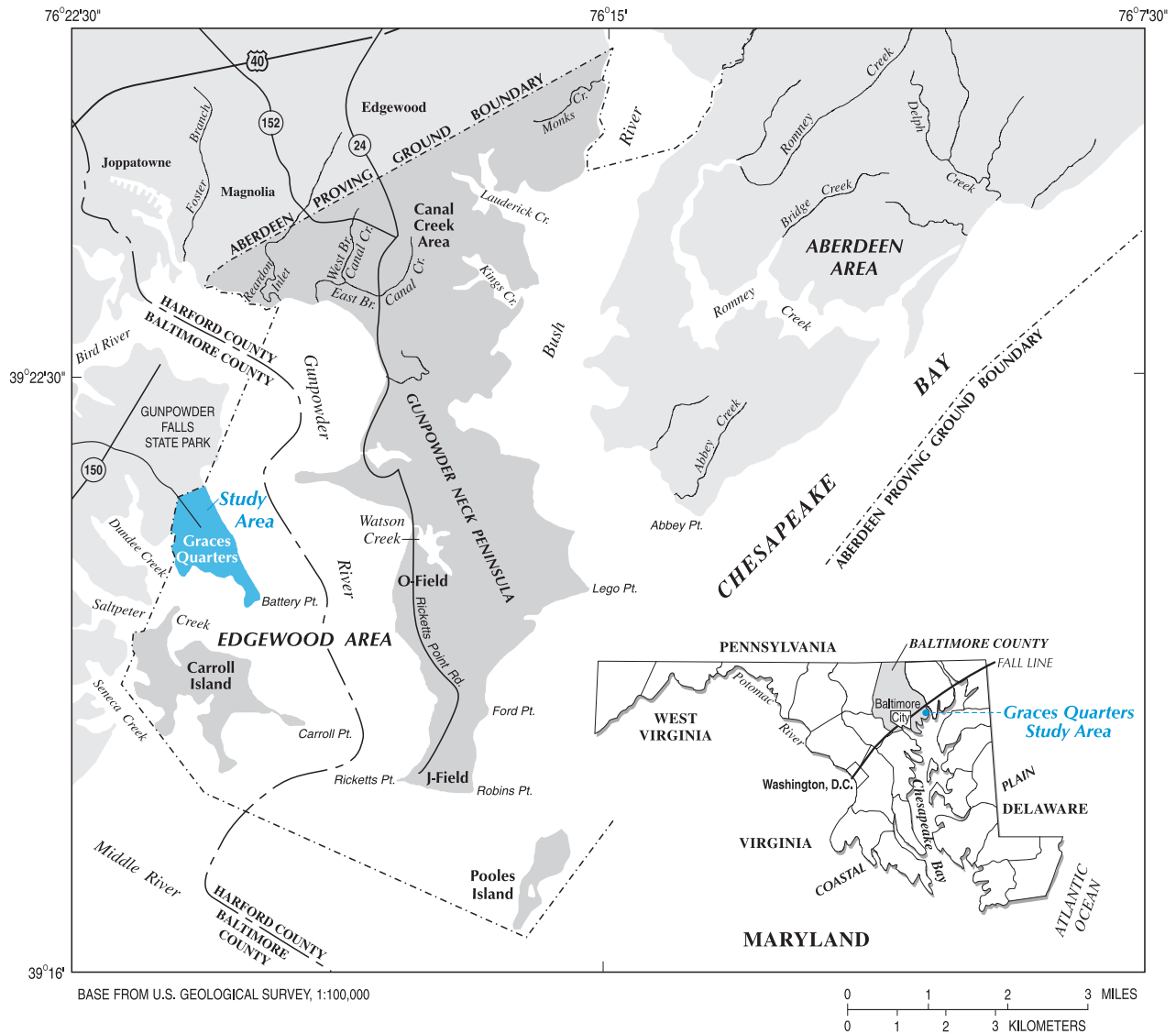


Figure 1. Location of Graces Quarters study area, Aberdeen Proving Ground, Maryland.

Introduction

Graces Quarters is located in the Edgewood Area of Aberdeen Proving Ground (APG), Baltimore County, Maryland (fig. 1), and was used as an open-air test site for chemical agents and munitions from the late 1940s to about 1971. Testing and disposal activities during this time resulted in ground-water contamination at Graces Quarters. Because ground-water contamination at this site degrades the waters of the State of Maryland, APG investigated the feasibility of remediating ground water at Graces Quarters.

Background

In 1977–78, Graces Quarters was investigated as part of an environmental survey of the Edgewood Area (Nemeth and others, 1983). This study resulted in the U.S. Environmental Protection Agency (USEPA) issuing a Resource Conservation and Recovery Act (RCRA) permit (MD3–21–002–1355) in 1986. The RCRA permit required that a hydrogeologic assessment be done at Graces Quarters.

The U.S. Geological Survey (USGS) began a study to collect the data needed for a hydrogeologic assessment of Graces Quarters in October 1986, at the request of the Environmental Management Office of APG, U.S. Department of Defense. The purpose of the hydrogeologic assessment was to collect hydrologic data in the vicinity of solid waste management units to provide a framework to

characterize any release and movement of contaminants. The hydrogeologic assessment also provided information about chemical-agent test sites, including the type of chemical agent tested and the period during which testing took place.

Much of what is known about historical testing activities at Graces Quarters is described in the RCRA Facility Assessment for the Edgewood Area (Nemeth, 1989), and in Tenbus and Phillips (1990). Hydrogeologic data collected from 1987 through spring 1989 can be found in Ham and others (1991). Interpretations of the hydrogeology and water quality of Graces Quarters from data collected during the hydrogeologic assessment can be found in Tenbus and Blomquist (1995).

In February 1990, the Edgewood Area of APG was placed on the USEPA National Priority List. Since that time, the Edgewood Area studies have been under Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) guidelines. The data and reports from the hydrogeologic assessment were used to help scope the Remedial Investigation/Feasibility Study (RI/FS) at Graces Quarters.

The RI/FS at Graces Quarters was designed to verify and characterize environmental contamination at the study sites, to assess the associated potential risks to human health and welfare and to the environment, and to propose and describe alternative remedial actions that will mitigate confirmed environmental contamination at each site where remediation is deemed necessary (Dames & Moore, Inc., 1993, p. 1–5). Remedial Investigation work included four rounds of ground-water sampling, two rounds of surface-water sampling, one round of soil and sediment sampling, and well installation and hydrogeologic interpretation (Dames & Moore, Inc., 1998a).

In 1996, USGS published the results of a ground-water modeling study of the Graces Quarters area (Tenbus and Fleck, 1996). Further work by USGS, Dames & Moore, Inc., and Hazardous Waste Remedial Actions Program (HAZWRAP) in 1996–97 indicated and confirmed that the 1996 modeling effort was based on an incorrect conceptual model of the hydrogeology of Graces Quarters. In the original conceptual model, the surficial and middle aquifers at Graces Quarters were thought to be separated by a continuous confining unit (Tenbus and Fleck, 1996, fig. 3). Although the middle aquifer was thought to be uncontaminated, the simulations suggested a high potential for transport of ground water from contaminated areas of the surficial aquifer to the middle aquifer within approximately 10 years. This result prompted a follow-up study by USGS to investigate solute-transport processes at Graces Quarters. The follow-up analysis of hydrogeologic and water-quality data from wells and direct-push probes for the solute-transport model revealed the possibility that the upper confining unit was not continuous, and that some of the direct-push probe samples that were contaminated were actually from the middle aquifer rather than from the surficial aquifer as originally thought. This possibility

meant that the middle aquifer was already contaminated at the time the data were collected (1995). If this were true, the extent of the contamination in the middle aquifer was not known, and additional work would be needed to characterize the plume.

The conflicting conceptual models were critically examined by USGS, APG, HAZWRAP, and Dames & Moore, Inc., and a plan was developed for a targeted effort to determine if the middle aquifer actually was contaminated. This additional ground-water investigation (Dames & Moore, Inc., 1998b) confirmed that the upper confining unit was not continuous and that the middle aquifer was contaminated. The study also determined the extent of contamination in the middle aquifer and provided information on ground-water head gradients, conduits for ground-water flow between the surficial and middle aquifers, and hydraulic conductivity information for the middle aquifer.

Once the plume in the middle aquifer was characterized, it became necessary to re-evaluate the potential remedial measures. A natural attenuation study (Dames & Moore, Inc., 1997) was initiated to determine if monitored natural attenuation would suffice as all or part of the remedial action for ground water at Graces Quarters. The USGS solute-transport modeling effort (described in this report) is designed to assist in the evaluation of remedial alternatives that include natural attenuation or enhanced bioremediation as components of the remedial effort.

Purpose and Scope

This report presents the results of numerical simulations involving three-dimensional solute transport of chlorinated hydrocarbons in ground water in the central part of Graces Quarters. The hydrogeology of Graces Quarters is described, along with model construction and calibration processes, and information about flow and transport that was learned during the calibration process. Simulations to test various concepts about contaminant sources and degradation rates and pathways are presented, as are the results of forward simulations of multi-species solute transport with and without removal of the contaminant sources.

Description of Study Area

APG is located on the western shore of the Chesapeake Bay in Harford and Baltimore Counties, Maryland (fig. 1). The land area of APG is about 30,000 acres (Nemeth, 1989, p. 1) and consists primarily of peninsulas and islands. Graces Quarters is a small (476 acres) peninsula in the southern part of the Edgewood Area of APG (fig. 1). Graces Quarters is surrounded by estuaries. No perennial or intermittent streams are present on the peninsula, but part of the land area is wetland (Tenbus and Fleck, 1996, p. 4). Precipitation in the area is about 44 in/yr (inches per year), and the climate is temperate.

Graces Quarters is located within the Atlantic Coastal Plain Physiographic Province, which consists of unconsolidated deposits of sand, silt, and clay underlain by crystalline rock (Tenbus and Fleck, 1996, p. 4). The unconsolidated sediment at Graces Quarters is mainly

Cretaceous (Crowley and others, 1976) and is classified as part of the Potomac Group (Otton and Mandel, 1984, p. 10). The Potomac Group is continental in origin and most likely was deposited in the flood plains of rivers and in lakes and swamps (Vokes, 1957, p. 47–48). Depth to bedrock in the Graces Quarters area is more than 300 ft (feet) (Bennett and Meyer, 1952, pl. 5).

Acknowledgments

The authors wish to thank the following people for their contributions to this report. Donald Green of the U.S. Army Environmental Conservation and Restoration Division, Aberdeen Proving Ground, provided administrative assistance and project guidance. Timothy Llewellyn, Sarah Forman, Scott Morgan, and Carol Mowder of URS Corporation (formerly Dames & Moore, Inc.), and George DeLong of Advanced Infrastructure Management Technologies participated in many technical discussions and provided much of the data on which this report is based. Michael Senus of the U.S. Geological Survey assisted in some of the hydrogeologic interpretations in this report.

Hydrogeology

An understanding of the hydrogeology of Graces Quarters is integral to the successful simulation of solute-transport processes within the ground-water flow system. The hydrogeologic framework of Graces Quarters is complex, and simulations must be based on a model that accounts for the most important aspects of the hydrogeology. The hydrogeology on which the solute-transport simulations are based is described below. Locations of hydrogeologic sections are shown on figure 2.

Aquifers and Confining Units

The aquifers that have been encountered at Graces Quarters during the hydrogeologic investigations of the site include a surficial aquifer, a middle aquifer, and a lower aquifer (fig. 3). Definition of the characteristics of these aquifers and their associated confining units has been an ongoing process since USGS began installing observation wells and geologic test holes in late 1987. The current (2001) understanding of the configuration of the aquifers and confining units is presented below.

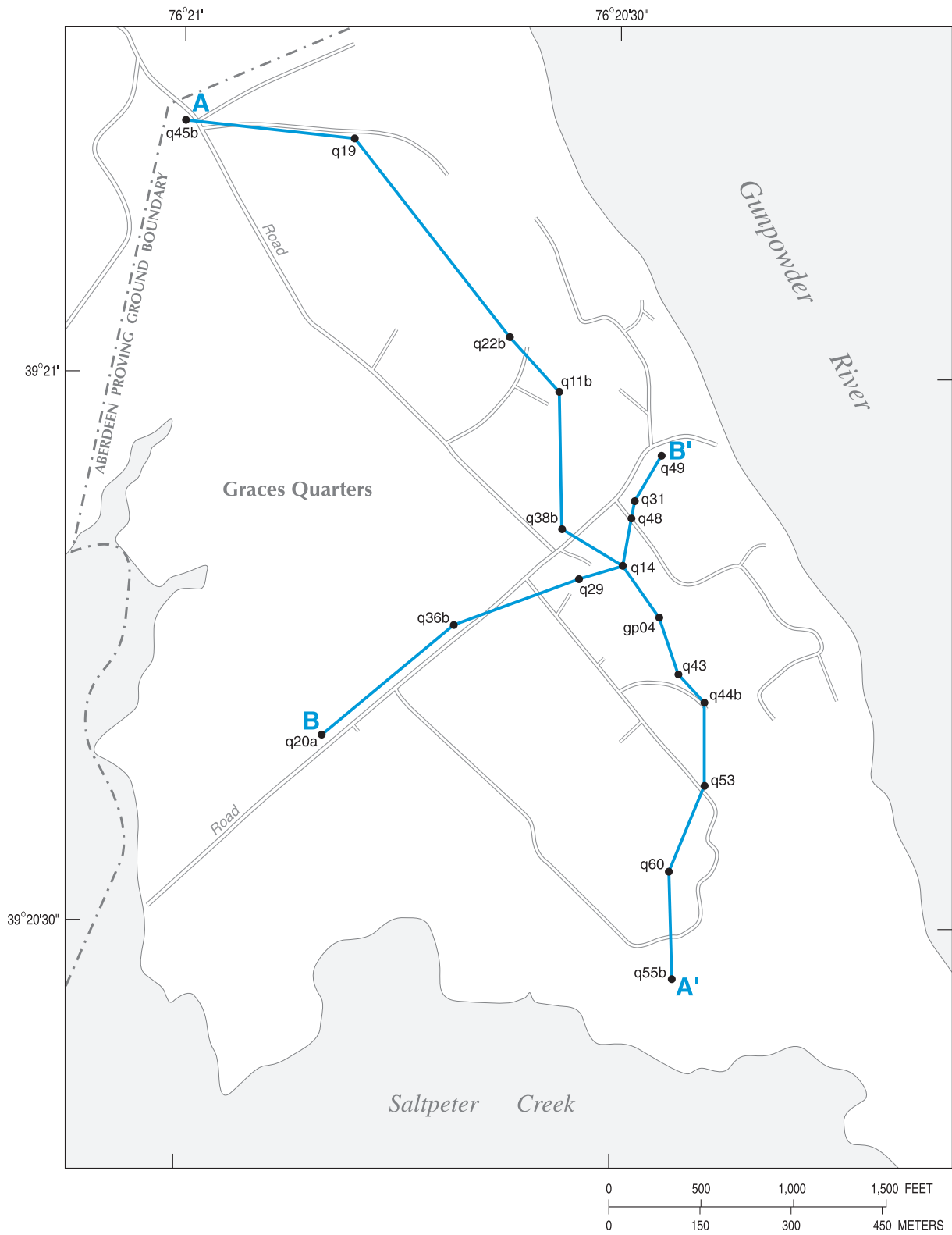
The uppermost aquifers on Graces Quarters are the surficial aquifer and the middle aquifer (fig. 3). Neither of the aquifers is continuous for the entire length of the peninsula, and both are interconnected in the south-central part of Graces Quarters where the ground water is contaminated. Although there is some interconnection between the surficial and middle aquifers, they have historically been treated as two separate aquifers (Tenbus and Fleck, 1996, p. 6). The surficial and middle aquifers are not present in the northern part of Graces Quarters; a massive clay confining unit dominates the shallow subsurface in that area (fig. 3). The lower aquifer is present beneath the massive clay in the

northern part of the peninsula. The lower aquifer may be continuous from the northern to the southern part of Graces Quarters, but the connection is not certain because of the distances involved, the lack of data, and the complexity of the subsurface stratigraphy.

Earlier work by USGS indicates that the lower aquifer in the northern part of Graces Quarters is not hydraulically connected with the surficial or middle aquifers (Tenbus and Blomquist, 1995, p. 41–49; Donnelly and Tenbus, 1998, p. 10–14). Hydraulic connection between the lower aquifer and the middle or surficial aquifers in the south-central part of Graces Quarters also is unlikely. A confining unit was encountered at the bottom of the middle aquifer in each of the wells that were drilled to characterize the middle aquifer (Dames & Moore, Inc., 1998b). At the one site where wells are screened in both the middle and lower aquifers (designated as well q38b, figs. 2 and 3), a head difference of 1.9 to 3.5 ft between the aquifers was measured over a wet and dry season in 1997 (Dames & Moore, Inc., 1998b, Appendix G), indicating a lack of connection between these aquifers. This contrasts with an area of the surficial and middle aquifers where the hydraulic connection is good (site is designated as well q44b, figs. 2 and 3). The head difference in these wells over the same time period was essentially zero (Dames & Moore, Inc., 1998b, Appendix G).

The configuration of the aquifers and confining units is an important factor controlling the overall pattern of ground-water flow at Graces Quarters. In the northern part of the peninsula, the surficial aquifer is either very thin or non-existent, and the middle aquifer is not present. The thick clay layer (fig. 3) and poorly transmissive aquifer material keeps water levels in the surficial aquifer (where it exists) well above sea level. Toward the central part of Graces Quarters, the surficial aquifer begins to thicken and the middle aquifer exists, but the aquifers are separated in most places by a confining unit. Farther south, the confining unit between the surficial and middle aquifers is missing in some locations, providing a recharge area for the middle aquifer and a conduit for contaminant transport from the surficial aquifer to the middle aquifer.

It is likely that ground-water flow in the surficial and middle aquifers at Graces Quarters is local, and the flow paths are short. The combination of the hydraulic barrier to the north (the thick clay layer), the localized recharge area, and the presence of large estuaries surrounding Graces Quarters effectively isolates the surficial and middle aquifers in the central and southern parts of the peninsula from the influence of the regional ground-water flow system. Because the extent of the middle aquifer beneath the estuaries is unknown, it is possible that the middle aquifer is part of a regional aquifer system that subcrops at Graces Quarters. It is known, however, that the middle aquifer is thin at the southernmost well on the peninsula (fig. 3), and that the hydraulic gradient between the surficial and middle aquifers in the southern part of Graces Quarters appears to be upward (Dames & Moore, Inc., 1998b, tables 4–3 and 4–4).



EXPLANATION

- A — A'** TRACE OF HYDROGEOLOGIC SECTION
- q55b •** OBSERVATION WELL AND IDENTIFICATION NUMBER

Figure 2. Location of hydrogeologic sections through Graces Quarters, Aberdeen Proving Ground, Maryland.

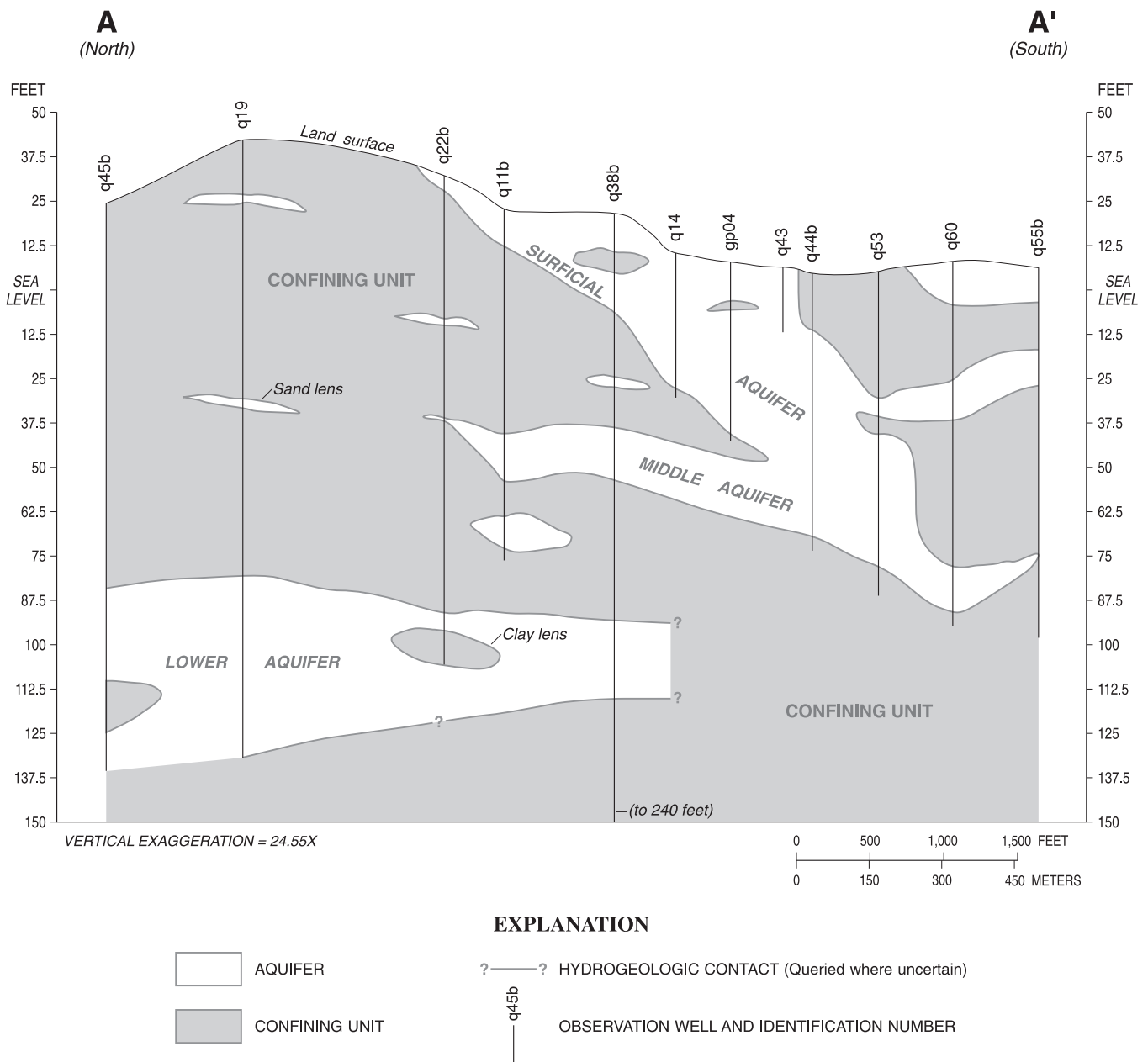
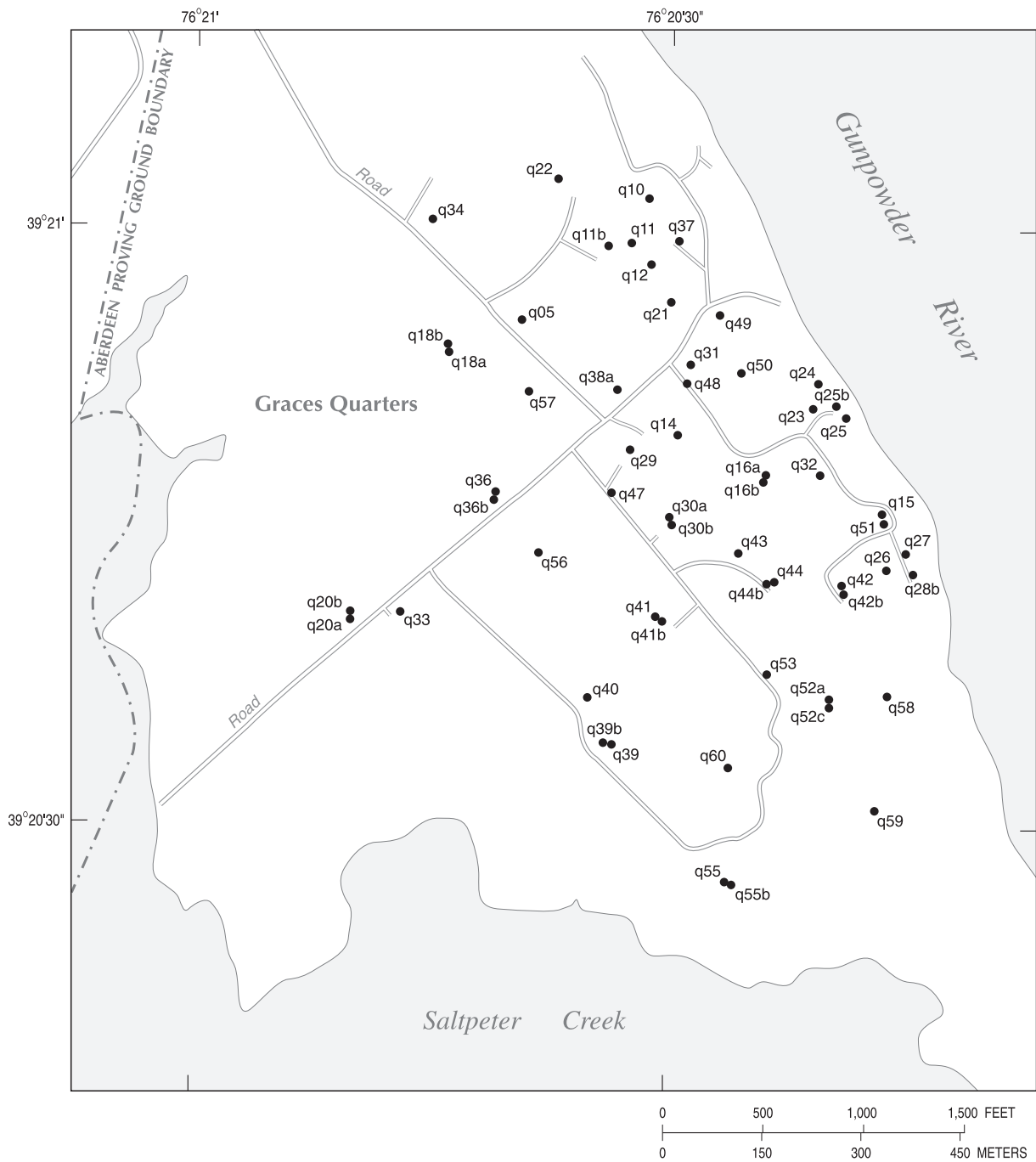


Figure 3. Section A-A' showing hydrogeologic units at Graces Quarters, Aberdeen Proving Ground, Maryland. (Refer to figure 2 for location of section.)

Hydraulic Head and Ground-Water Flow

Because the lower aquifer shows no signs of contamination and is not known to be hydraulically connected to the other aquifers at Graces Quarters, this section focuses on the hydrology of the surficial and middle aquifers. Information about hydraulic head in the aquifers at Graces Quarters from as early as 1987 is available (Ham and others, 1991, table 8). Interpretations of hydraulic gradients and seasonal and tidal fluctuations of hydraulic head are presented in Tenbus and Blomquist (1995), Tenbus and

Fleck (1996), and Donnelly and Tenbus (1998). Most of the current wells in the southern and central part of Graces Quarters were not installed until the mid-1990s, however, so the head information collected prior to then has some limitations. The later wells were installed by Dames & Moore, Inc. (1995, 1998b) to improve the understanding of the hydrogeology of the southern and central part of the peninsula. Locations of selected wells that are screened in the surficial or middle aquifers at Graces Quarters are shown in figure 4.



EXPLANATION

q55b ● OBSERVATION WELL AND IDENTIFICATION NUMBER

Figure 4. Location of selected wells in the surficial and middle aquifers, Graces Quarters, Aberdeen Proving Ground, Maryland.

The hydraulic head configuration in the surficial and middle aquifers at Graces Quarters is largely controlled by the hydrogeologic framework of the peninsula. In the surficial aquifer (fig. 5), head is highest in the northern part of Graces Quarters because the hydraulic conductivity of the aquifer is very low, and the underlying clay unit is present at elevations above sea level. Ground water in this area is isolated from the estuaries by poorly transmissive sediment, so head remains high. The area of high head to the north, another similar area to the east, and the presence of wetlands to the south of the peninsula cause the primary direction of ground-water flow in the surficial aquifer to be to the south (fig. 5).

Although the hydraulic gradient in the surficial aquifer shows certain ground-water flow directions, it is important to remember that ground-water flow is a three-dimensional process. Ground water will flow downgradient, but in a heterogeneous (non-uniform) environment such as the one at Graces Quarters, high hydraulic gradient may be indicative of areas where ground-water flow is minimal because it cannot easily pass through the sediment. Additionally, ground-water flow may be downward or upward rather than lateral, depending on the presence or absence of confining units that retard ground-water flow, or highly transmissive preferential flow pathways.

In one or more areas of Graces Quarters, the confining unit between the surficial and middle aquifers is missing (fig. 3). This provides a conduit for ground-water flow from the surficial to the middle aquifer. This conduit appears to affect the configuration of hydraulic head in the surficial aquifer (fig. 5), in that head in certain wells near the conduit is lower than in other surrounding wells. The conduit also appears to have a great effect on the hydraulic head distribution in the middle aquifer (fig. 6). Hydraulic head contours in the middle aquifer seem to be somewhat concentric around the area in the southeastern part of the peninsula where the confining unit is missing, indicating that this is a recharge area for the aquifer. The contours are somewhat elongated to the northwest and southeast, which may be the result of higher hydraulic conductivity along this axis.

Recharge and discharge processes can be inferred from the hydraulic head configuration and from the characteristics of the Graces Quarters peninsula. Recharge to the surficial and middle aquifers results from precipitation. Because the surficial and middle aquifers are isolated from the regional ground-water flow system by the clay unit to the north (fig. 3), precipitation that falls beyond the boundary of Graces Quarters will not affect the recharge on site. Most of the recharge to the surficial and middle aquifers is seasonal and usually occurs in late winter through the spring. This is evident from ground-water hydrographs presented in Ham and others (1991, figs. 13–23) and Donnelly and Tenbus (1998, fig. 6). Discharge from both of the aquifers is probably into the wetlands at the fringes of the peninsula (fig. 4) or into the estuaries, because the middle aquifer appears likely to pinch out to the south of Graces Quarters

(fig. 3), and hydraulic gradients between the surficial and middle aquifers are upward in some well clusters near marshes (wells q28 and q28b; q52a and c; and q55a and b) (Dames & Moore, Inc., 1998b, Appendix G). In addition, head in a well in the surficial aquifer near a wetland (q28) has been observed above land surface (Tenbus and Blomquist, 1995, p. 37), indicating an upward component of flow in that aquifer near the perceived discharge area.

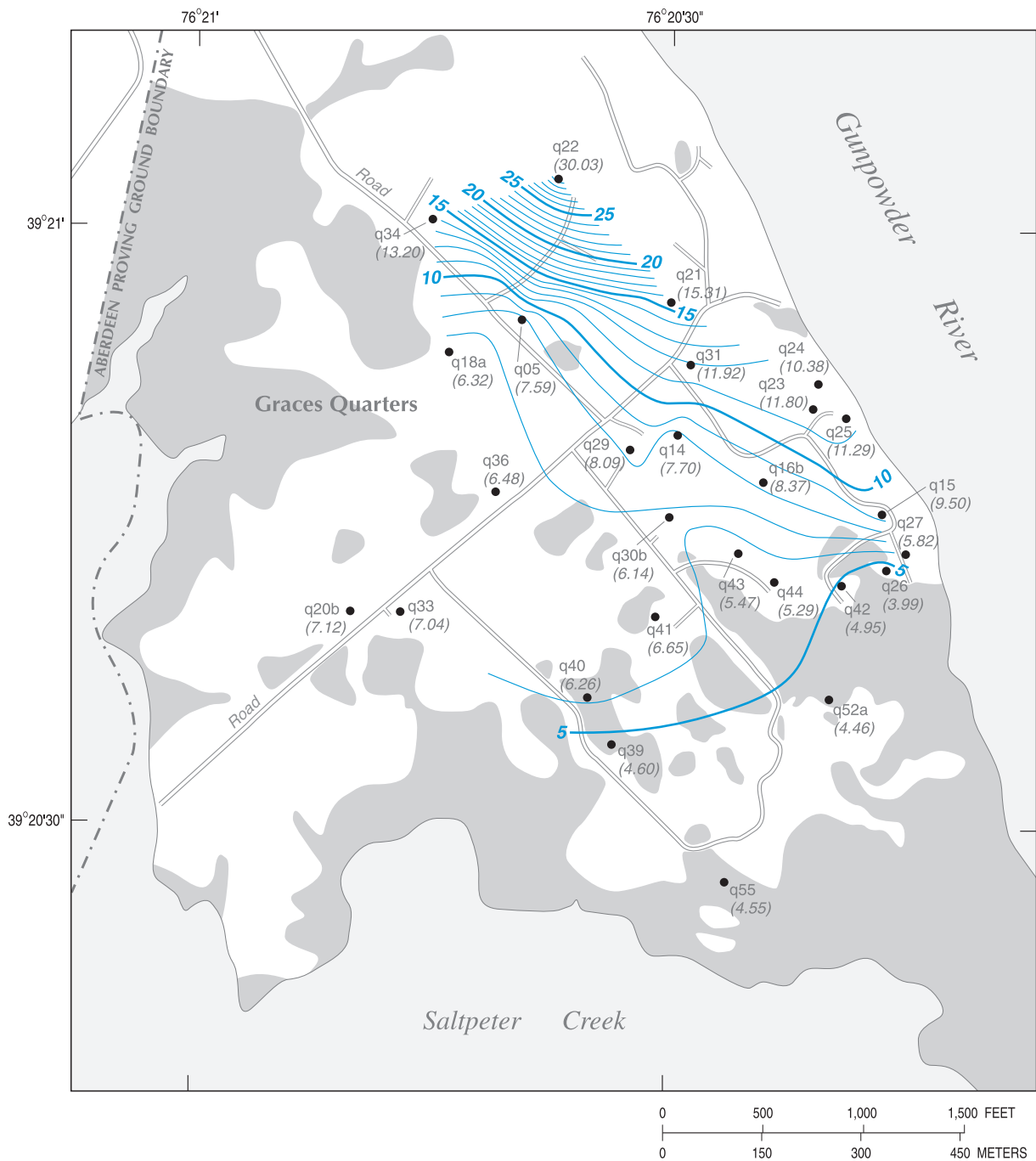
Inferences about ground-water flow in the surficial and middle aquifers are based on the following data. A physical boundary (thick clay layer) for the aquifers has been defined to the north, and likely discharge areas (wetlands and estuaries) are present to the west, south, and east. A large number of wells and well clusters are available to determine the vertical boundaries and hydraulic gradients within and between the aquifers, and slug tests were performed on many of the wells to determine hydraulic conductivity (Dames & Moore, Inc., 1996, table 4–7; 1998b, table 4–5; Tenbus and Blomquist, 1995, table 3 and p. 49).

Distribution of Contaminants in Ground Water

Along with the hydraulic information discussed previously, another indicator of ground-water flow direction and velocity is the distribution of contaminants within the surficial and middle aquifers. Direct-push probes (fig. 7), which are not permanent sampling points but can be used to obtain lithologic and water-quality samples, were used in conjunction with wells to determine the configuration of the contaminant plumes in the surficial and middle aquifers (figs. 8 and 9).

The contaminant plumes shown in figures 8 and 9 consist of the chlorinated solvents 1,1,2,2-tetrachloroethane, trichloroethene, carbon tetrachloride, and chloroform (Dames & Moore, Inc., 1998b). Records documenting their use on Graces Quarters have not been found, but each of these highly chlorinated compounds might have been released at the site during the historical testing period. Three of the compounds (trichloroethene, carbon tetrachloride, and chloroform) are common industrial solvents. The other compound (1,1,2,2-tetrachloroethane) was the solvent in a decontaminating agent known as DANC (decontaminating agent non-corrosive). Solutions of DANC reportedly were 90 to 95 percent 1,1,2,2-tetrachloroethane (Nemeth, 1989, p. 177).

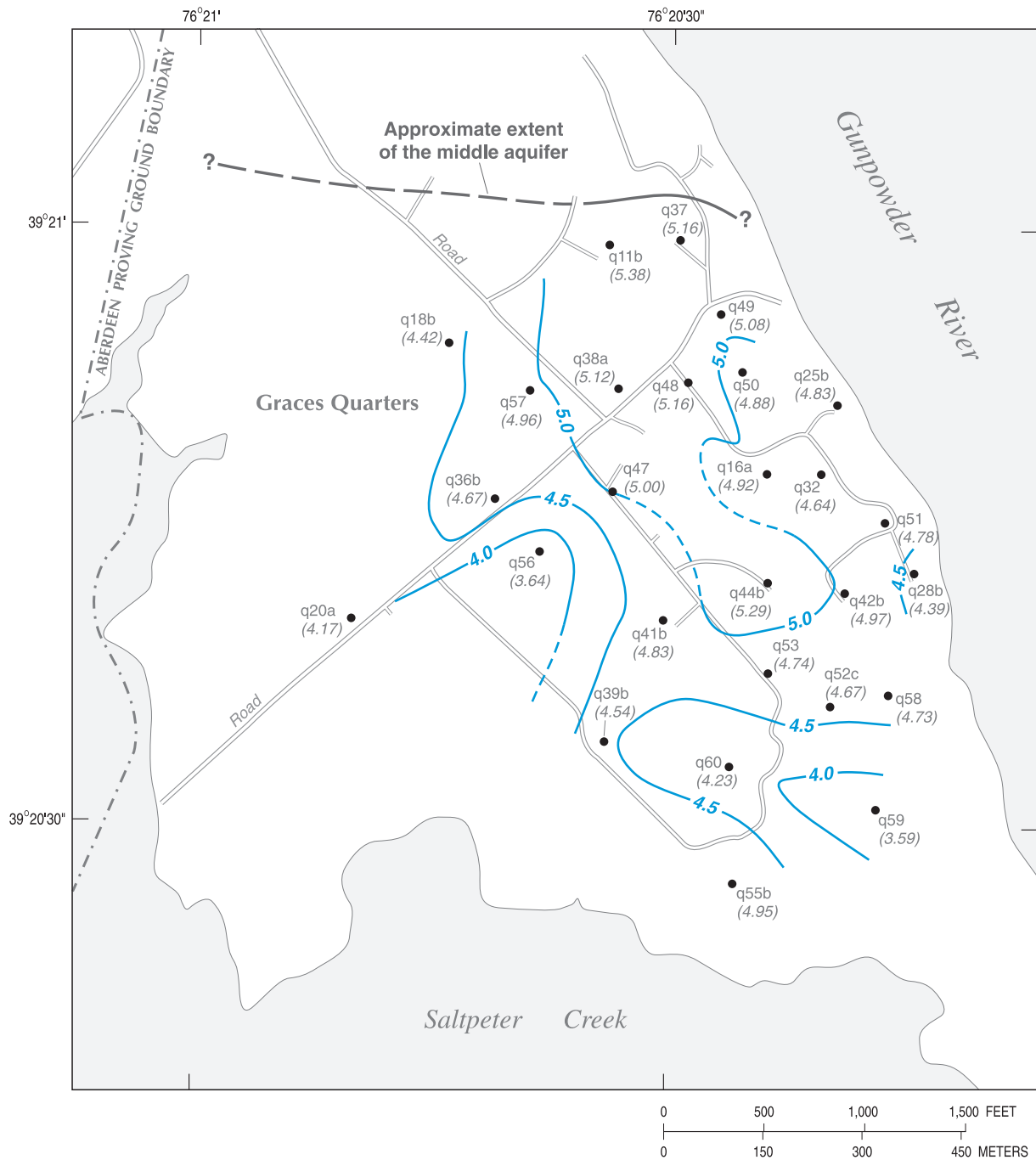
It is likely that DANC and other decontaminating agents were the original source of the chlorinated solvents in the plume at Graces Quarters. Nemeth (1989, p. 178) indicates that DANC was widely used at APG, and that it was used in decontamination studies on Graces Quarters (Nemeth, 1989, p. 145). A number of empty drums and at least one empty DANC container were found at a dump site near the contaminated area at Graces Quarters (Nemeth, 1989, p. 496). Lorah and Vroblesky (1989, p. 69) state that chlorine or bleach dissolved in carbon tetrachloride were common decontaminating agents used at APG, so this represents a possible source for the contaminants in ground water at Graces Quarters. The use of chloroform and dye during test activities was documented at nearby



EXPLANATION

- WETLAND
- 5** WATER-LEVEL CONTOUR (Shows approximate water-level contour in the surficial aquifer. Contour interval 1 foot. Datum is sea level.)
- q55 (4.55) ● OBSERVATION WELL AND IDENTIFICATION NUMBER (Number in parentheses is hydraulic head, in feet.)

Figure 5. Hydraulic head in the surficial aquifer, Graces Quarters, Aberdeen Proving Ground, Maryland, April 21, 1997.



EXPLANATION

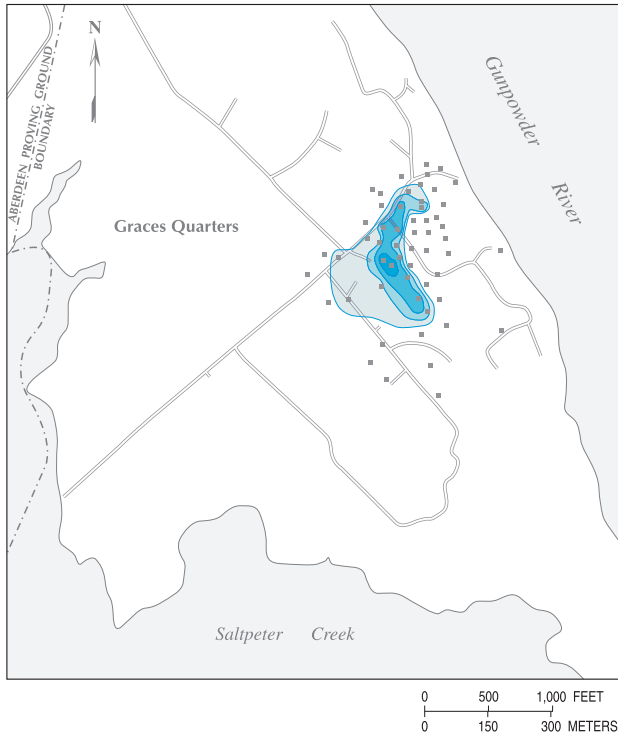
- 5.0 — WATER-LEVEL CONTOUR (Shows approximate water-level contour in the middle aquifer. Dashed where inferred. Contour interval 0.5 foot. Datum is sea level.)
- q55b (4.95) ● OBSERVATION WELL AND IDENTIFICATION NUMBER (Number in parentheses is hydraulic head, in feet.)

Figure 6. Hydraulic head in the middle aquifer, Graces Quarters, Aberdeen Proving Ground, Maryland, April 21, 1997.

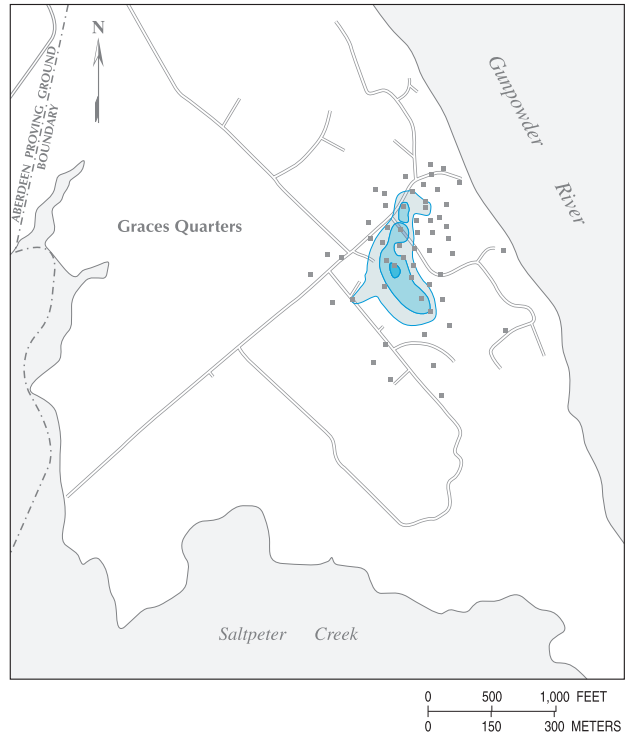


Figure 7. Location of direct-push sampling points, Graces Quarters, Aberdeen Proving Ground, Maryland, summer 1995.

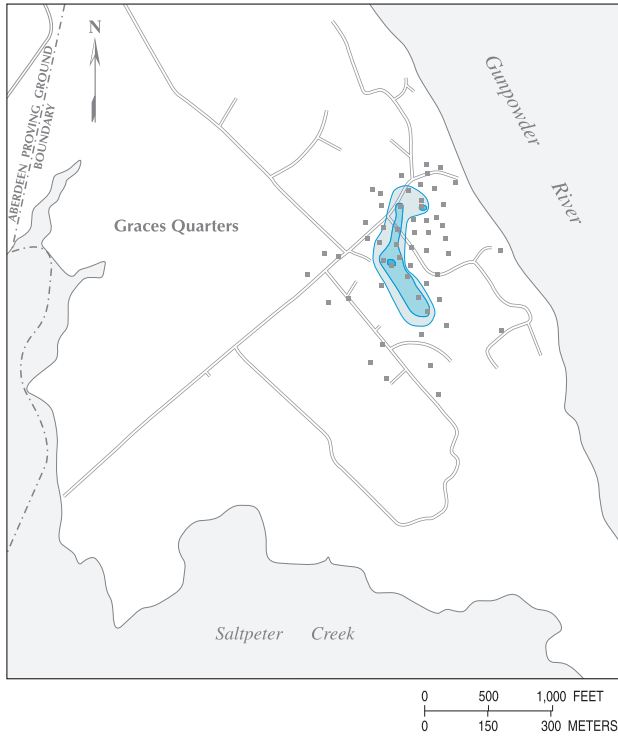
**1,1,2,2-TETRACHLOROETHANE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



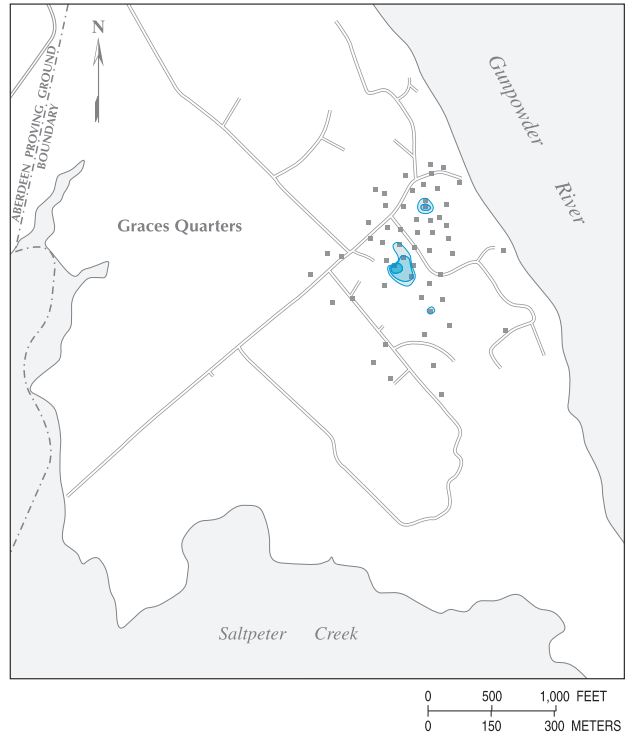
**TRICHLOROETHENE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CARBON TETRACHLORIDE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CHLOROFORM CONCENTRATIONS,
IN MICROGRAMS PER LITER**



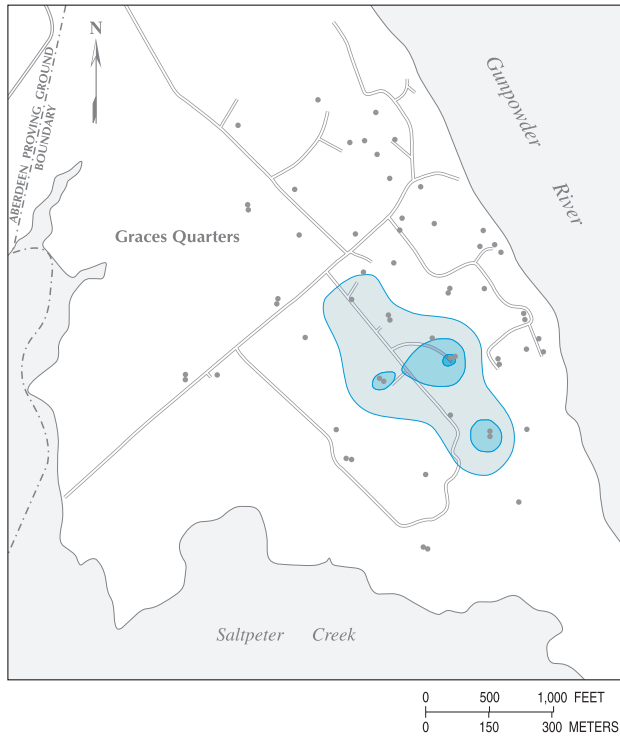
EXPLANATION

CONTAMINANT CONCENTRATION, IN MICROGRAMS PER LITER

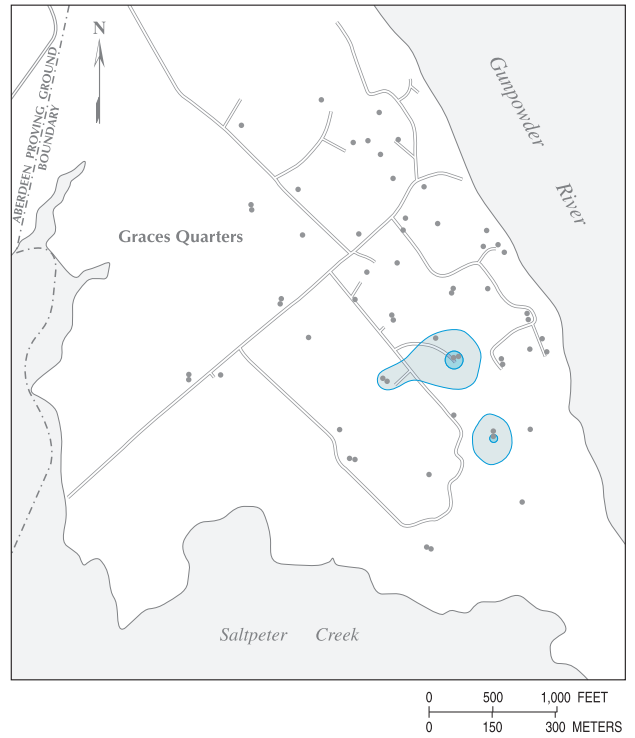


Figure 8. Horizontal extent of the 1,1,2,2-tetrachloroethane, trichloroethene, carbon tetrachloride, and chloroform plumes in the surficial aquifer from direct-push probe samples, Graces Quarters, Aberdeen Proving Ground, Maryland, summer 1995 (modified from Dames & Moore, Inc., 1998b).

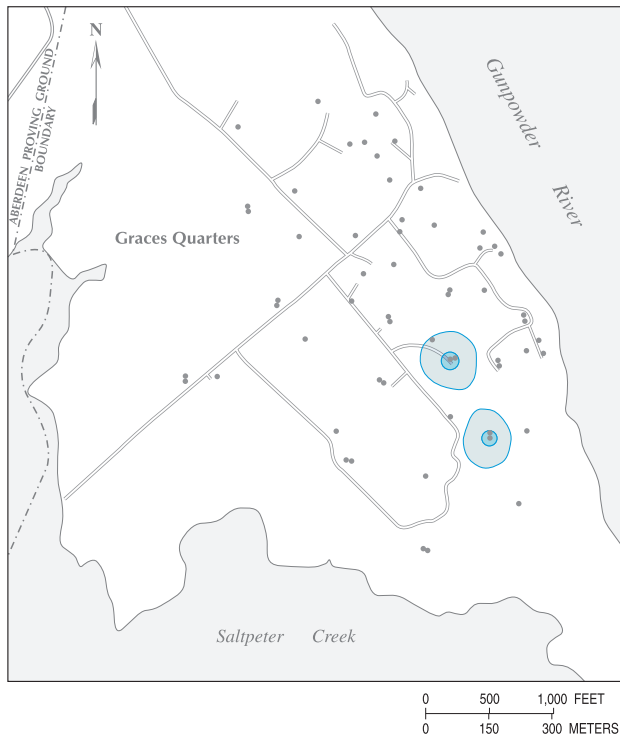
**1,1,2,2-TETRACHLOROETHANE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



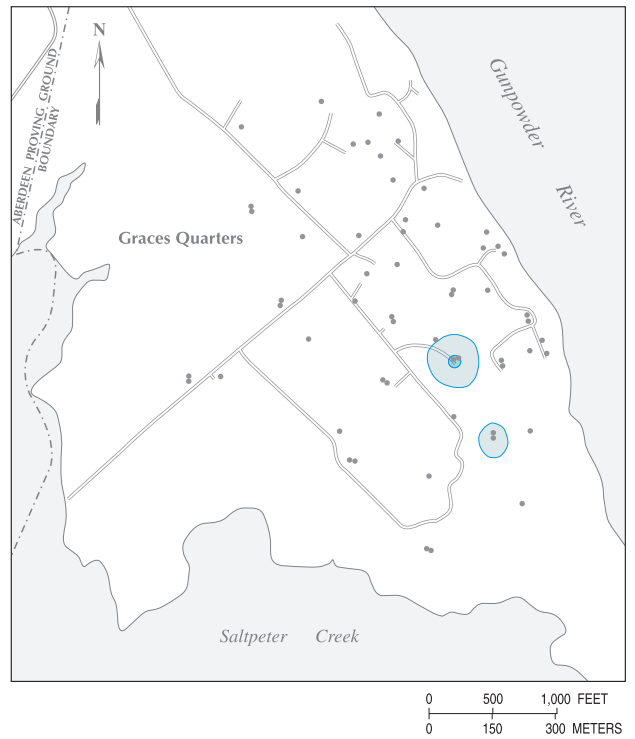
**TRICHLOROETHENE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CARBON TETRACHLORIDE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CHLOROFORM CONCENTRATIONS,
IN MICROGRAMS PER LITER**



EXPLANATION



Figure 9. Horizontal extent of the 1,1,2,2-tetrachloroethane, trichloroethene, carbon tetrachloride, and chloroform plumes in the middle aquifer from observation-well samples, Graces Quarters, Aberdeen Proving Ground, Maryland, spring and summer 1997 (modified from Dames & Moore, Inc., 1998b).

Carroll Island (Tenbus and Phillips, 1996, table 1). Some or all of the chloroform and trichloroethene in the Graces Quarters plume might also have resulted from the degradation of carbon tetrachloride and 1,1,2,2-tetrachloroethane, respectively.

The amount of time that contaminants have been transported is an unknown aspect of the plume, but the site history provides some important clues about the probable age of the contaminants. Graces Quarters was used as a test site from the late 1940s to 1971. In the early 1950s, Graces Quarters and neighboring Carroll Island (fig. 1) became the primary areas of chemical testing at APG (Nemeth, 1989, p. 141). Aerial photography of Graces Quarters during the 1950s shows evidence of significant testing activities during that decade (Dames & Moore, Inc., 1998a, p. 1–4). Written documentation of test activities at Graces Quarters is sparse until 1964, but Nemeth (1989, p. 150) provided a table of known chemicals released from July 1964 until December 1971 (see also Tenbus and Blomquist, 1995, table 2). Nemeth's table contains no mention of the release of chlorinated solvents or DANC. It is possible that chlorinated solvents were used from 1964–71 and not noted, but that seems unlikely for two reasons. First, the table contains a listing for an herbicide along with the chemical warfare agents, which indicates that all chemicals were included. Second, a similar list for Carroll Island (Tenbus and Phillips, 1996, table 1) from the same time period notes the release of sodium hydroxide (a decontaminating agent), and carbon tetrachloride (a chlorinated solvent), as well as innocuous chemicals such as talcum powder, further indicating that the lists are complete. The combination of written historical records and aerial photographs constrains the likely time of release of chlorinated solvents at Graces Quarters to the period between the early 1950s and 1964.

Several aspects of the plume configuration are useful for making inferences about the source area and some of the factors such as advection and dispersion that control contaminant transport. Considerable uncertainty exists about the contaminant source. Historical use of the contaminated area as an open-air test site for chemical warfare agents might indicate a diffuse source of contaminants from possible applications of chemicals to large areas of the surface. Another likely scenario is that multiple point sources of contaminants would come from application of chemicals to relatively small areas or objects such as vehicles. The distribution of contaminants in the surficial aquifer (fig. 8) seems to indicate that one or more point sources along the axis of the plume are most likely. It is possible that residual dense non-aqueous phase liquid (DNAPL) is present in the surficial aquifer, but the surficial aquifer has been sampled intensively, and the presence of large amounts of DNAPL is not indicated. Small amounts of DNAPL bound up in the sediment pores, however, could account for the continuous sources of chlorinated organic compounds in ground water at the site.

Contaminants in the middle aquifer at Graces Quarters (fig. 9) appear to have resulted from aqueous transport of

contaminants from the surficial aquifer through breaches in the confining unit. The highest detected concentrations in the middle aquifer are at well q44b (fig. 9), which is close to the area where the confining unit is missing (fig. 3). The concentrations of total volatile organic compounds along a hypothetical flow path between the central part of the plume in the surficial aquifer to well q44b in the middle aquifer decrease in the downgradient direction, indicating that aqueous transport would be sufficient to account for the concentrations in solution in the middle aquifer. No direct-push probe sampling points are located adjacent to the screen in well q44b, however, so the possibility of residual DNAPL near that well has not been ruled out.

Simulation of Ground-Water Flow and Transport of Chlorinated Hydrocarbons

Numerical simulation of a ground-water flow system with computer models is an important and useful tool in many hydrogeologic investigations. Numerical models can be used to predict the consequences of a proposed action, and they can also be useful in interpreting the controlling factors of a particular hydrogeologic setting (Anderson and Woessner, 1992, p. 4). Numerical simulation was used at Graces Quarters for both of these purposes. Forward simulations were run to examine some of the possibilities for future transport of contaminants with and without removal of the contaminant sources. In addition, the process of designing, calibrating, and testing the model provided insight into some of the factors that affect ground-water flow and solute transport in the study area.

The ground-water flow and solute-transport models for Graces Quarters were developed as part of intensive studies of the hydrogeology and water quality of the site. Large quantities of data have been generated and interpreted. Because the data and interpretations showed that the flow system is complex, efforts were made from the beginning to incorporate some of the complexity into the model design. An example of this was the use of pre-processing software to generate spatially variable hydraulic conductivity arrays by interpolation from known points such as wells and direct-push probes. Care was taken throughout the modeling process to determine the level of detail necessary to include in the models, with complexity added as it became needed.

In spite of all the complexity that was incorporated into the simulations, it is inherently impossible to simulate a hydrogeologic system without error. Hydrogeologic parameters are inferred by boring holes in the ground, making observations and measurements, and generalizing that information over a larger volume of the earth. Some of the observations and inferences (such as hydraulic conductivity, boundary conditions, and layer configurations) are incorporated into a computer program that solves equations to produce simulated values that should match observations and measurements (such as hydraulic head in

an aquifer). The quality of the match between the calculated and measured values is frequently used as an indicator of how “good” a simulation is. Unfortunately, simulations can appear to be accurate even though they are based on incomplete or incorrect information.

Model Design and Boundary Conditions

Ground-water flow, solute transport, and reactive solute transport were simulated using several different modeling packages. Each of the packages that was used is publicly available and well documented. Ground-water flow was simulated using MODFLOW and MODFLOW-96 (McDonald and Harbaugh, 1988; Harbaugh and McDonald, 1996), the USGS modular three-dimensional finite-difference ground-water flow model. Solute-transport modeling was accomplished initially through MOC3D (Konikow and others, 1996), which is a USGS three-dimensional method-of-characteristics solute-transport model. Subsequent solute-transport modeling was done with MT3D (Zheng, 1990), a three-dimensional solute-transport model that can be used in a manner similar to MOC3D. MT3D was chosen to facilitate multi-species reactive solute-transport modeling with RT3D (Clement, 1998). RT3D is an extension to MT3D that simulates degradation of parent compounds and formation of daughter compounds along with the standard solute-transport parameters of advection, dispersion, and sorption.

Pre-processing of input data and post-processing of output files for the models was an integral part of developing and calibrating the simulations used in this study. The use of pre-processors enabled the interpolation of values from known data points (such as direct-push probe locations and observation wells) onto the model grid. Interpolation capabilities allowed heterogeneity in the spatial distribution of simulated hydraulic conductivity and variations in top and bottom elevation of model layers among the grid nodes. This was an especially powerful tool at Graces Quarters because of the high density of data points and the complexity of the hydrogeologic framework. Most of the pre-processing of MODFLOW and MOC3D input was done with graphical user interfaces developed by Shapiro and others (1997) and Hornberger and Konikow (1998) that used Argus Numerical Environments. Subsequent pre- and post-processing of MODFLOW, MT3D, and RT3D was done with GMS, the U.S. Department of Defense ground-water modeling system (Brigham Young University, 1998).

Ground-water flow at Graces Quarters was simulated with a six-layer, fully three-dimensional finite-difference MODFLOW model that represented the surficial and middle aquifers and their associated confining units. The finite-difference model grid (fig. 10) consisted of a 96-row by 98-column array of uniformly spaced 100- by 100-ft grid nodes oriented in a north-south direction. The top and bottom elevations of layers were explicitly defined in the model and are spatially variable. The top of layer 1 is the water-table elevation; all of the other layer elevations at each grid node were determined using interpolated data from hydrogeologic contacts described in borehole logs.

The layering scheme for the model was designed to be consistent with the site hydrogeology and to be appropriate for numerical accuracy in the simulation of the flow and transport processes. The general structure of the model layers was determined by examining hydrogeologic sections (Dames & Moore, Inc., 1998b, figs. 4–1 through 4–5). Because of the lenticular nature of the sediment that comprises the hydrogeologic framework of Graces Quarters, the thickness of the aquifers and confining units exhibits considerable spatial variability. Extreme variation in the thickness of model layers can cause numerical instability in ground-water flow models as well as problems with mass balance in solute-transport models. For this reason, it was decided that none of the layers would be designated as strictly an aquifer layer or a confining-unit layer. Instead, each layer would have spatially variable hydraulic properties that were consistent with the available data from boreholes and site characteristics. Top and bottom boundaries for layers were based on the elevations of hydrogeologic contacts, with each aquifer and confining unit consisting of one or more layers, depending on the unit thickness. An example of the layer configuration is shown in figure 11.

A data set was developed in which point values for the bottom elevation of each of the layers could be tabulated. Lithologic logs of boreholes (wells, direct-push probes, and test holes) from studies at Graces Quarters (Dames & Moore, Inc., 1995, 1996, 1998b; Ham and others, 1991) were assembled and used to set bottom elevations of the layers at each borehole location. Because each borehole at Graces Quarters has been geospatially referenced in three dimensions (map coordinates and elevation of land surface), data from the boreholes could be tabulated to provide a large number of point values that could be used to generate information for each of the model layers.

The initial entries for the data set included only the boreholes that encountered the bottom of the middle aquifer, which was to be the lower boundary of the ground-water flow and solute-transport models. The base of model layer 6 was set at the bottom of the middle aquifer in each of these boreholes. Bottom elevations for layers 1 through 5 were then determined for the same boreholes and entered into the data set. In addition, a Unified Soil Classification System (USCS) abbreviation (Casagrande, 1948) based on the one or two dominant soil classes included in each layer at each borehole was assigned and entered into the data set to help with the subsequent interpretation of hydraulic conductivity for the model.

Entering these initial data points provided a framework for the layering and USCS information from shallower boreholes. Hydrogeologic contacts in shallow boreholes were compared with those in the deeper ones that were initially entered, and the bottom elevations and USCS abbreviations for the number of layers encountered in each borehole were put into the data set.

An initial value of hydraulic conductivity at each borehole was entered for each layer that was encountered. Hydraulic conductivity values were obtained in two ways,

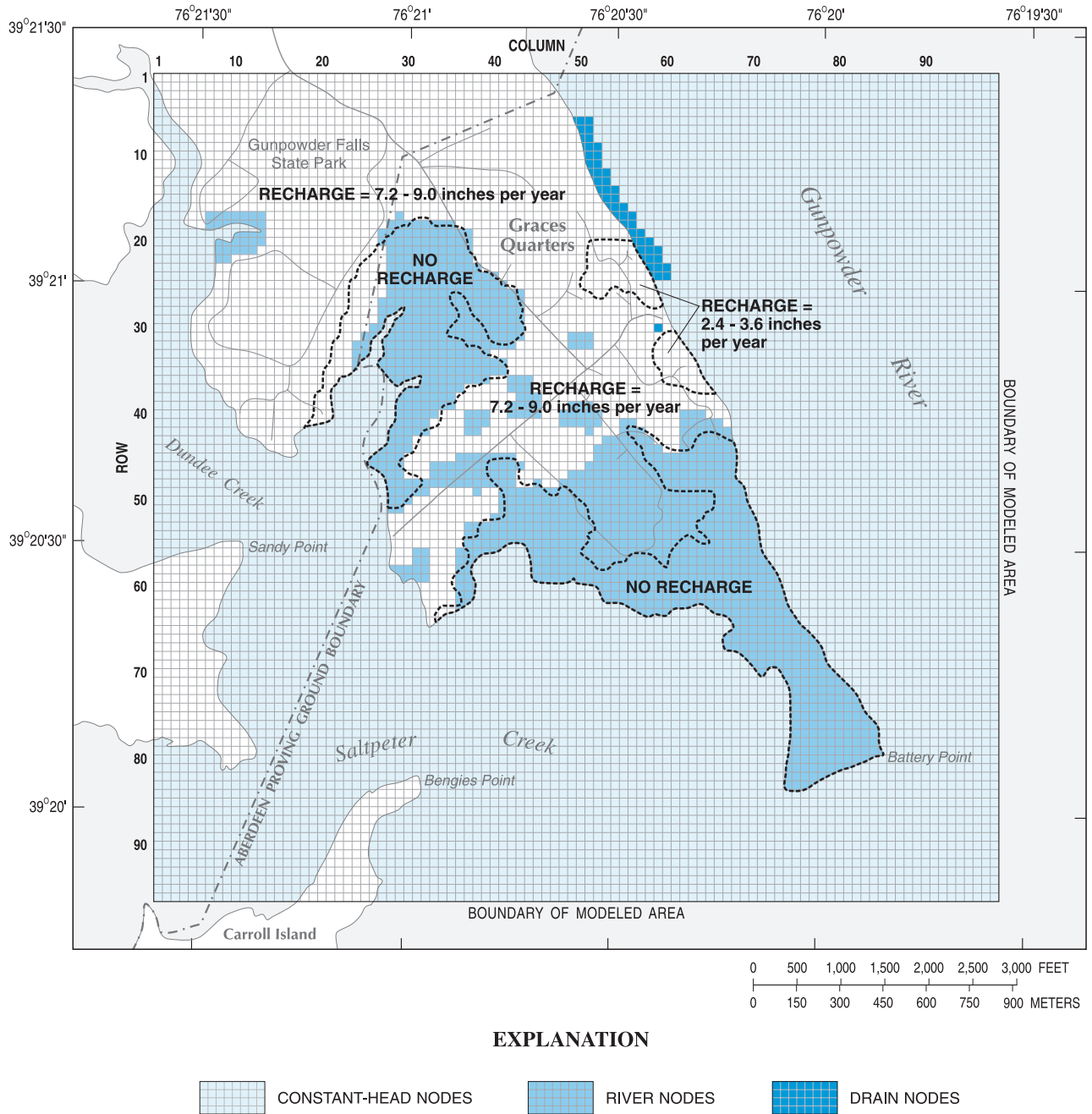


Figure 10. Grid location and simulated hydrologic features in layer 1 of the ground-water flow and solute-transport model in the Graces Quarters area, Aberdeen Proving Ground, Maryland.

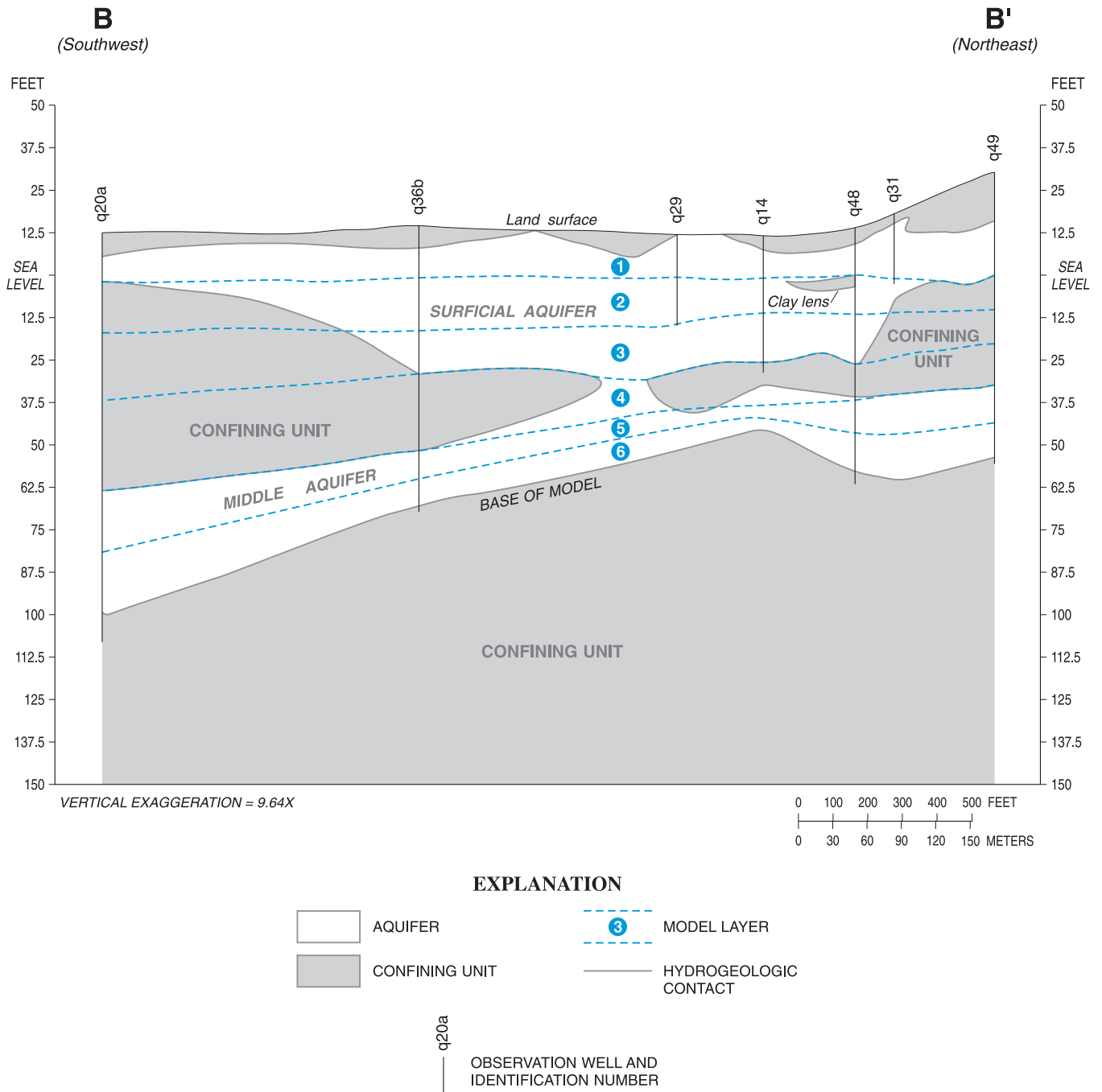


Figure 11. Hydrogeologic section B-B' showing aquifers, confining units, and model layers at Graces Quarters, Aberdeen Proving Ground, Maryland. (Refer to figure 2 for location of section.)

depending on the available data. First, if a well was screened in a given layer and hydraulic conductivity was determined from one of the slug tests or pumping tests that were done on site, this hydraulic conductivity value was assigned to the layer at that well. If those data were not available but lithologic information was recorded, an estimated value for hydraulic conductivity was entered based on the USCS abbreviations assigned to each layer encountered in the borehole. The protocol for determining initial hydraulic conductivity values from the USCS classification is described below.

The protocol is a modification of the one used in an earlier ground-water flow model at Graces Quarters (Tenbus and Fleck, 1996, table 3). A subset of the available USCS letter symbols (SP for well sorted sand, SM for silty sand, SC for clayey sand, ML for silt, and CL for clay) was assigned to or obtained from each of the different strata in the lithologic log of each borehole. Grain-size data for each model layer in a particular borehole formed the basis for a four-letter abbreviation that combined the USCS letter symbols of the one or two most prevalent soil classifications in the layer. For example, the abbreviation for a layer that consisted of well sorted sand at a particular borehole location would be SP-SP; a layer made up of alternating bands of silty sand and clay would be abbreviated as SM-CL. A hydraulic conductivity value was assigned to each USCS letter symbol. The hydraulic conductivity value for the model layer at each borehole location was calculated by doubling the first value, adding it to the second, and dividing the resulting sum by three to obtain a weighted average hydraulic conductivity. These point data were later interpolated onto the model grid using the pre-processing software.

Horizontal hydraulic conductivity entered into the model as point values (prior to calibration) ranged from 0.00005 to 68 ft/d (feet per day). The lowest value was entered at many borehole locations where clay was encountered throughout the model layer at that point. The highest value was entered at a single point and was based on the result of a slug test at well q20a (Tenbus and Blomquist, 1995, p. 49). Vertical hydraulic conductivity was routinely entered as a point value two orders of magnitude lower than the corresponding point value for horizontal hydraulic conductivity. Interpolation of horizontal and vertical hydraulic conductivity values was done by a proprietary inverse distance weighted interpolation within the pre-processing software (Argus Interware, Inc., Jericho, New York). This resulted in values at the grid nodes that were usually different from the point values entered at the boreholes. Care was taken during the modeling process to check the effects of interpolation and to ensure that the values used in the simulations were consistent with the available data.

Boundary conditions of the model were designed to reflect the current understanding of the ground-water flow system at Graces Quarters. Model boundaries were designed to be hydrogeologically accurate in the areas that affect ground-water flow in the central part of Graces Quarters,

where the surficial and middle aquifers are contaminated. Important boundary conditions (fig. 10) include constant-head nodes representing the estuaries that surround the peninsula, drain nodes representing seepage from a cliff face in the northeastern part of Graces Quarters (Tenbus and Fleck, 1996, p. 9), and river nodes that represent the wetlands that are prevalent on much of the peninsula (Tenbus and Fleck, 1996, fig. 2). All of these boundary conditions were set only in the uppermost layer of the model to be consistent with the natural features in the area. The upper boundary of the model is the water table, and the base of the model is a no-flow boundary set at the elevation of the bottom of the middle aquifer.

Some simulated boundary conditions do not accurately reflect the hydrogeology of the area, but they were considered unimportant to the simulations and appear to have negligible effects on the results. The extreme edges of the model grid are simulated in MODFLOW as no-flow boundaries. The model grid at Graces Quarters (fig. 10), however, is very large compared to the area of contaminated ground water, and a large number of constant-head cells are present in layer 1 between the active nodes and the edge of the grid for most of the model area. The large areas of constant-head nodes in layer 1 were designed to simulate the effects that the relatively constant water levels in the estuaries have on ground-water flow at Graces Quarters. The northern boundary of Graces Quarters was also simulated with constant-head cells (fig. 10) set at the same elevation as the estuary, even though this is a land area and not an estuary. Although this may not be the most accurate way to simulate this boundary, the surficial and middle aquifers are not present in the area, so this boundary was not considered to be important to the simulations. Simulated head configurations in the area were checked throughout the calibration process to ensure that they were consistent with available data and the topography of the area.

Recharge to the aquifers underlying Graces Quarters was simulated as a constant flux of 0 to 9 in/yr into the active cells in layer 1. Areal zonation of recharge (fig. 10) similar to that in Tenbus and Fleck (1996) was incorporated into the model based on topography, the presence of fine-grained sediment within or above the surficial aquifer, the presence of wetlands, and field observations of overland flow. Because the surficial and middle aquifers at Graces Quarters are recharged locally and are not areally extensive, no regional ground-water flow into or out of the model at the lateral grid boundaries was simulated. Discharge from the aquifers was simulated as seepage from the drain cells at the cliff face, outflow to the river cells representing wetlands, or outflow to the constant-head cells representing the estuaries. Evapotranspiration processes, which could be seasonally important in parts of the Graces Quarters flow system, were not explicitly simulated. Instead, the ground-water flow system was simulated as steady state, with any effects of evapotranspiration generalized into the recharge flux.

Simulation of solute transport at Graces Quarters required knowledge or estimations of several factors beyond

those required for the simulation of ground-water flow. Information about source locations and strength had to be input, and values for effective porosity, dispersivity, retardation or sorption, and rates of contaminant degradation had to be estimated or obtained. In addition, various contaminant degradation pathways had to be identified and evaluated. Considerable uncertainty exists about most of the information that is needed for the simulation of solute transport. For this reason, most of the initial estimates of the solute-transport parameters were adjusted during the calibration process to try to obtain realistic simulations based on reasonable assumptions. Because of the uncertainties, the solute-transport simulations are non-unique; that is, a number of other different simulations could probably produce similar results. The implications of these uncertainties are discussed in later sections of the report.

Simulated source locations were based on characteristics of the observed plume in the surficial aquifer (fig. 8) such as shape (the plume is narrow in the upgradient direction) and the location of highly contaminated samples from direct-push probes. Contaminant sources were simulated in the model by injecting small fluxes of water with high concentrations of contaminants into appropriate model cells using the MODFLOW well package and MT3D or RT3D point sources. Initial values for source strength were estimated from contaminant concentrations and refined during calibration. An effective porosity value of 0.25 was chosen based on discussion in Zheng and Bennett (1995, p. 46–48) and information about on-site porosity (Dames & Moore, Inc., 1998b, table 4–2). Dispersivity was determined empirically during the calibration process, as discussed in Zheng and Bennett (1995, p. 50). Inferences about the effects of sorption in the ground-water flow system at Graces Quarters were based on contaminant fate and transport studies in the Canal Creek area of APG (Lorah and others, 1997; Lorah and Vroblesky, 1989). Information about contaminant degradation rates and pathways was obtained from the preliminary results of a natural attenuation study at Graces Quarters (T. Llewellyn, URS Corp., written commun., 1999).

Model Calibration

The ground-water flow and solute-transport models at Graces Quarters were calibrated using a systematic approach of adjusting hydraulic and transport parameters until the calibration targets for hydraulic head and concentration of 1,1,2,2-tetrachloroethane were matched by the simulations within an acceptable margin of error. The general approach to calibrating the models was to (a) calibrate the ground-water flow model to closely match measured hydraulic head values from wells in the surficial and middle aquifers; (b) run advective solute-transport simulations (no dispersivity or sorption coefficients), making adjustments to hydraulic parameters so that the centroid of mass of the simulated contaminants was transported to locations in the surficial and middle aquifers that are similar to those in the observed plume; and (c) calibrate the solute-transport model using parameters such as dispersivity and sorption to closely match

measured concentrations of samples from direct-push probes and observation wells in the surficial and middle aquifers. Throughout the calibration process, care was exercised to ensure that the calibration adjustments were within reasonable limits and that the available data were used to the fullest extent.

The interpolation capability of the modeling pre-processor was used during much of the calibration process. Because layer elevations and hydraulic parameters such as horizontal and vertical hydraulic conductivity were entered into the model primarily as point values within each layer, calibration adjustments were made by altering the point values and interpolating the adjusted data set onto the model grid. In this way, heterogeneity was included in the model and maintained during calibration. The point data in each layer were adjusted within reasonable limits, and the effects of the interpolation routines on the spatial representation of hydraulic parameters were checked between each run. Great care was taken to ensure that the interpolations were realistic, and that they were consistent with the available data. In the final stages of calibration, changes were made on a cell-by-cell basis within the model so that the effects would be smaller and the results of changes more predictable.

The objective of the calibration was to closely simulate the hydraulic head and ground-water flow fields in the surficial and middle aquifers at Graces Quarters. The calibration process was an attempt to minimize statistical differences between measured and simulated values of hydraulic head and the concentration of 1,1,2,2-tetrachloroethane in ground water without making large alterations to model features that are based on measured values and observations about the hydraulics of the system. The large quantities of available data had the dual effect of complicating the calibration process (by revealing the complexities of the flow and transport system) and making the results more accurate (by providing many measured values to help constrain the calibration).

The calibration was primarily a trial-and-error process, which makes it somewhat subjective. Several steps, however, were taken to ensure the quality of the calibration. First, quantitative calibration targets were set for a large number of data points both inside and outside of the contaminated area, and statistical comparisons were made between the measured and simulated data. Second, the models were calibrated to hydraulic head and contaminant concentration, which provided an extra constraint on the simulated ground-water flow field. Third, the long history of hydrologic investigations at Graces Quarters was used as a framework with which to assess the qualitative aspects of the calibration. Finally, reasonable ranges of possible flow and transport parameters were maintained through careful attention to the available data and the literature.

Hydraulic head The calibration targets for hydraulic head in the surficial and middle aquifers at Graces Quarters (table 1) were obtained from a synoptic water-level survey conducted on April 21, 1997, by Dames & Moore, Inc.

Table 1. Measured and simulated head in observation wells, Graces Quarters, Aberdeen Proving Ground, Maryland

[No., number; col., column; measured head and simulated head in feet above sea level; measured head represents conditions on April 21, 1997; simulated head represents values calculated by the model that was calibrated to hydraulic head and contaminant distribution]

Well no. (fig. 4)	Location in model (row, col., layer)	Measured head ^A	Simulated head	Absolute difference between measured and simulated head
q05	30,46,2	7.59	8.23	0.64
q10	24,53,1	9.38	10.48	1.10
q11	26,52,2	5.62	9.98	4.36
q11b	26,51,5	5.38	5.47	.11
q12	27,53,3	11.83	9.09	2.74
q14	36,54,3	7.70	9.39	1.69
q15	40,64,2	9.50	7.56	1.94
q16a	38,58,6	4.92	5.04	.12
q16b	38,58,1	8.37	8.93	.56
q18a	31,43,1	6.32	6.85	.53
q18b	31,43,5	4.42	4.20	.22
q20a	45,38,5	4.17	3.19	.98
q20b	45,38,1	7.12	6.28	.84
q21	29,54,1	15.31	14.48	.83
q22	23,48,1	30.03	29.13	.90
q23	34,61,1	11.80	12.53	.73
q24	33,61,1	10.38	10.83	.45
q25	35,62,1	11.29	10.83	.46
q25b	34,62,5	4.83	4.26	.57
q26	43,65,2	3.99	4.58	.59
q27	42,65,2	5.82	5.12	.70
q28b	43,66,6	4.39	3.75	.64
q29	37,52,1	8.09	9.37	1.28
q30a	40,54,1	7.17	8.25	1.08
q30b	40,54,3	6.14	7.51	1.37
q31	32,55,1	11.92	13.50	1.58
q32	38,61,4	4.64	4.88	.24
q33	45,40,1	7.04	7.13	.09
q34	25,42,1	13.20	11.98	1.22
q36	39,45,1	6.48	6.42	.06
q36b	39,45,6	4.67	4.31	.36
q37	26,54,5	5.16	5.42	.26
q38a	33,51,6	5.12	5.05	.07
q39	51,51,1	4.60	5.22	.62
q39b	51,50,6	4.54	3.68	.86
q40	49,50,1	6.26	5.69	.57
q41	45,53,1	6.65	6.37	.28
q41b	45,53,6	4.83	4.83	0
q42	44,62,4	4.95	4.79	.16

Table 1. Measured and simulated head in observation wells, Graces Quarters, Aberdeen Proving Ground, Maryland—Continued

Well no. (fig. 4)	Location in model (row, col., layer)	Measured head ^A	Simulated head	Absolute difference between measured and simulated head
q42b	44,62,6	4.97	4.66	0.31
q43	42,57,1	5.47	5.84	.37
q44	43,59,1	5.29	5.89	.60
q44b	43,59,6	5.29	5.23	.06
q47	39,51,5	5.00	5.04	.04
q48	33,55,6	5.16	4.96	.20
q49	30,56,6	5.08	4.82	.26
q50	33,57,6	4.88	4.70	.18
q51	40,64,5	4.78	4.17	.61
q52a	50,62,1	4.46	4.76	.30
q52c	50,62,6	4.67	4.15	.52
q53	48,58,6	4.74	4.54	.20
q55a	58,57,2	4.55	4.71	.16
q55b	58,57,6	4.95	2.95	2.00
q56	42,47,6	3.64	4.27	.63
q57	34,47,5	4.96	4.82	.14
q58	49,65,6	4.73	3.70	1.03
q59	55,64,5	3.59	2.95	.64
q60	52,57,6	4.23	3.90	.33

^A. Dames & Moore, Inc., 1998b, Appendix G.

(1998b, Appendix G). This data set was chosen for the quantitative comparisons of simulated versus measured head because it included all of the wells that are within and adjacent to the contaminated area at Graces Quarters. Earlier data sets (such as those in Ham and others, 1991) were useful for determining seasonal trends and long-term averages, but because they did not include many of the wells in the contaminated area (which were installed during the remedial investigation in the mid–1990s), they were less useful for quantitative comparisons. Disadvantages of the April 1997 calibration data set were that some of the wells within the model domain were excluded (the excluded wells generally were far from the contaminated area and therefore were not important to the simulations) and that the heads that were measured tended to be higher than the long-term average because of the wet spring in 1997.

The calibration data set for hydraulic head (table 1) was one of only two synoptic water-level surveys that included all of the wells that were important to the transport simulations. The second water-level survey, which also was obtained from Dames & Moore, Inc. (1998b, Appendix G), was performed on August 28, 1997. The second data set was not included in the calibration because it was strongly affected in the area of interest by evapotranspiration (water levels in several wells near the marshes were below sea level

in August 1997), which was not simulated in the ground-water flow model. On the basis of information from monthly and continuous water-level measurements at Graces Quarters (Ham and others, 1991), it did not seem that averaging the two data sets would allow for a more accurate or useful calibration data set than using the single wet-season synoptic survey.

Statistical comparison between the simulated and measured values in table 1 was done to quantitatively assess the calibration match. The mean error (ME), root-mean-squared error (RMSE), and the mean absolute error (MAE) provide ways to determine the overall goodness-of-fit between the simulated and measured values. Each of these statistics is calculated within the GMS modeling environment using the following formulas (Brigham Young University, 1998, p. 14–20):

$$ME = \frac{1}{n} \sum_{i=1}^n (h_c - h_o)_i$$

$$MAE = \frac{1}{n} \sum_{i=1}^n |(h_c - h_o)_i|$$

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (h_c - h_o)_i^2}$$

where

- n = the number of observation points,
- h_c = the computed (simulated) value, and
- h_o = the observed (measured) value.

For the calibrated ground-water flow model the, ME between simulated and measured head for the 58 wells listed in table 1 was -0.03 ft. The MAE for the 58 wells was 0.69 ft, and the RMSE was 1.02 ft. Measured head in the calibration data set (table 1) ranged from 3.59 ft in well q59 to 30.03 ft in well q22. The RMSE was less than 4 percent of this range. The model greatly overestimated head in one well (well q11, table 1) and underestimated head in another well (q12; see fig. 4 for well locations). These wells are located in layers 2 and 3 in the model, in an uncontaminated area. Hydraulic connections in this area are difficult to determine; anomalous water levels in this area were discussed in earlier studies (see Tenbus and Blomquist, 1995, p. 36–37). Numerous attempts during the calibration process to reduce the errors in this area did not produce satisfactory results, so it is unclear what could be done to improve the calibration in this part of the model. These wells might be screened in sand lenses that are hydraulically isolated from the aquifer in the contaminated area. The poor calibration in this area is not believed to adversely affect the simulation of solute transport.

Distribution of 1,1,2,2-tetrachloroethane The second part of the calibration was to run a relatively simple solute-transport simulation using the ground-water flow model that had been calibrated to hydraulic head. This step was necessary because advection is usually the controlling factor in solute transport, so good simulation of advection is extremely important. A continuous upgradient source of contaminant was injected into layer 1 of the model in an area that represented a likely source of contamination. A 40-year transport simulation (which would correspond to a contaminant release sometime in the late 1950s) was done in an attempt to match the shape and characteristics of the existing plume. Initial runs indicated that calibrating the ground-

water flow model to hydraulic head alone was not adequate for the simulation of solute transport at Graces Quarters. Some aspects of the transport matched the observed plume—the plume shape in the upper model layers was similar, and a significant mass of solutes was transported into the middle aquifer. The biggest problem, however, was that the centroid of mass of the solute was transported into the middle aquifer in the wrong area, so the shape and transport characteristics of the simulated plume in the middle aquifer were very different from those of the observed plume.

For this reason, adjustments were made to horizontal and vertical hydraulic conductivity values in the model to change the transport pattern while maintaining a good hydraulic head calibration with the available data. The process involved careful analysis of the stratigraphy as represented by the lithologic logs of wells and direct-push probes, and careful adjustment to the model. Essentially, adjustments were made where they were necessary and could either be consistent with the available data or did not conflict with available data. Calibration runs that simulated 60 years of transport (with solutions printed at 5-year intervals) allowed for the analysis of temporal and spatial effects of changes to model parameters between runs.

After the ground-water flow model was calibrated and the simulation of advective transport was refined to the point where the overall plume characteristics were approximated, additional factors were evaluated to try to improve the simulation of solute transport. This part of the calibration involved evaluation of various configurations of source locations and strength; estimates of dispersivity, sorption, and decay were obtained and adjusted; and hydraulic parameters such as porosity and hydraulic conductivity were refined. Quantitative and qualitative calibration criteria were used to evaluate the relative merit of changes that were made during the process. Changes were evaluated based on (1) the overall statistical goodness-of-fit between the simulated concentration and calibration target at all of the sampling locations; (2) the overall shape of the simulated plume compared with the shape of the plume as shown in figures 8 and 9; (3) the simulated and measured concentration at individual sampling points; and (4) the degree of certainty or uncertainty in the value of the factor that was changed.

Because uncertainty exists about the factors involved in simulating solute transport, it was important to use any available information to try to constrain the values that were selected for the final simulations. Site-specific data were used whenever possible, but other sources of information, such as parameter values and estimation techniques that have been reported in literature, were also used to assist in the calibration process.

As previously discussed, some information about the sources of chlorinated hydrocarbons in ground water at Graces Quarters can be inferred from site data, but various aspects of the simulated sources were adjusted during the calibration process to help match the calibration targets. In general, the contaminant sources in the simulations were

placed in areas where high concentrations (in the thousands of micrograms per liter) of chlorinated hydrocarbons were detected in samples from wells or direct-push probes. The exact locations of the simulated sources, however, were adjusted as part of the calibration process. Additionally, the amount of simulated contaminant that was injected at each source was subject to calibration.

Dispersion in a solute-transport simulation provides a mechanism to account for factors such as diffusion, the tortuosity of individual flow paths, and heterogeneities in porous media that cause particle velocities to deviate from the average seepage velocity. Although the interpolation techniques used in the ground-water flow simulation for Graces Quarters allowed for the incorporation of some of the hydraulic heterogeneity in the system, it is impossible to incorporate all of it for at least two reasons. First, only a small fraction of the heterogeneities can be identified even in an intensely studied area (Zheng and Bennett, 1995, p. 50). Second, much of the heterogeneity in a ground-water flow system is at a smaller scale than can be represented by a grid cell. Additional factors such as temporal variations in recharge rates and source strength or location that affect solute transport (Goode and Konikow, 1990, p. 2,339) often are incorporated into simulations as dispersion. For these reasons, it is necessary to include dispersive transport in most solute-transport simulations.

Dispersive transport in a three-dimensional solute-transport model is usually simulated with three dispersivity coefficients—one for longitudinal dispersivity, which represents dispersion along the flow axis, and two for transverse dispersivities, which represent dispersion in the vertical and horizontal directions normal to the axis of flow. MT3D and RT3D allow the user to set a variable longitudinal dispersivity within each model layer, and to set the transverse horizontal and transverse vertical dispersivities for each layer as fractions of the longitudinal dispersivity. A common rule of thumb is that longitudinal dispersivity will be much larger than transverse horizontal dispersivity, which in turn will be larger than transverse vertical dispersivity (Zheng and Bennett, 1995, p. 247–249). This rule of thumb was used in the Graces Quarters simulations.

Sorption processes are difficult to characterize in many field situations. Different chemicals have different sorption properties, and the degree to which chemicals are sorbed can vary according to the types of sediment encountered. Sorption coefficients for the sediment at Graces Quarters were not determined from on-site field data or from laboratory experiments. Instead, qualitative information from Graces Quarters was used in conjunction with information from the literature and from similar sites nearby to estimate sorption values.

The sorption coefficient that is used to calculate a retardation factor in solute-transport modeling is proportional to the fraction of organic carbon within the subsurface sediment. In the aquifers underlying Graces Quarters, the fraction of organic carbon is thought to be small. In 32 sediment samples from a similar aquifer in the

Canal Creek area across the Gunpowder River from Graces Quarters, the median fraction of organic carbon was 0.000026 (Lorah and Vroblesky, 1989, p. 83), and the maximum was an order of magnitude higher (Lorah and Vroblesky, 1989, table 15). Other values in the literature (such as those in Domenico and Schwartz, 1998, table 12.7) and in later work in the West Branch Canal Creek area (Olsen and others, 1997, table 5) tend to be somewhat higher than the median reported by Lorah and Vroblesky (1989). Based on typical literature values and on published sediment/water partition coefficients (Schwille, 1988, Appendix I), sorption in the model was set so that the retardation factors for the constituent volatile organic compounds at Graces Quarters ranged from 1.2 (for chloroform) to 1.8 (for carbon tetrachloride). Retardation factors for 1,1,2,2-tetrachloroethane and for trichloroethene in the model were approximately 1.3.

The rate of *in situ* first-order decay of 1,1,2,2-tetrachloroethane at Graces Quarters also was used to assist in the solute-transport calibration. As with the other solute-transport parameters, the rate of decay can be difficult to quantify. At Graces Quarters, a natural attenuation study was done to help quantify the decay rates, and preliminary results suggested a half-life for 1,1,2,2-tetrachloroethane of about 27 years (T. Llewellyn, URS Corporation, written commun., 1999). The degradation pathways for natural attenuation were not clear, however, and the possibility still existed that no decay of chlorinated solvents was occurring in the aquifers. Initial calibration efforts incorporated the decay rate suggested by the natural attenuation study into the simulations, but the final calibration was done with no decay. Uncertainties in the degradation rates and pathways are discussed in a later section of this report.

The final calibration of the ground-water flow and solute-transport model was based on the ability of the model to simulate the measured concentrations (or concentrations that were adjusted as described below) at 58 observation wells and 101 direct-push probe sampling points (tables 2 and 3). The calibration results in tables 2 and 3 are based on a simulation in which a plume was generated to represent measured concentrations of 1,1,2,2-tetrachloroethane in ground water at Graces Quarters during the mid-1990s. The plume was generated by simulating 40 years of continuous injection of solute into six model cells, the locations of which were based on probable source areas—three cells in layer 1 (at row 31, columns 55 and 56, and at row 32, column 55), which are near well q31, and three cells in layer 3 (at row 33, column 54; at row 36, column 54; and at row 38, column 56), which are in areas where high concentrations of 1,1,2,2-tetrachloroethane were detected. The sources simulated the injection of a combined total of 0.0215 liters per day of water from the six model cells at a concentration of 2,610,000 µg/L (micrograms per liter), which is equal to the calculated effective solubility of 1,1,2,2-tetrachloroethane for a hypothetical DNAPL mixture with a mole fraction of 90 percent 1,1,2,2-tetrachloroethane and 10 percent trichloroethene. A longitudinal dispersivity

Table 2. Measured concentration, calibration target, and simulated concentration for observation wells, Graces Quarters, Aberdeen Proving Ground, Maryland

[No., number; col., column; ND, not detected; measured concentration, calibration target, and simulated concentration are in micrograms of 1,1,2,2-tetrachloroethane per liter of water. Calibration target was based on measured concentration; comparison of simulated concentration to calibration target provides a measure of the quality of the calibration. Absolute difference is between the simulated concentration and the calibration target]

Well no. (fig. 4)	Location in model (row, col., layer)	Measured concentration ^A	Calibration target	Simulated concentration	Absolute difference
q05	30,46,2	ND	0	0.1	0.1
q10	24,53,1	ND	0	0	0
q11	26,52,2	ND	0	.1	.1
q11b	26,51,5	ND	0	0	0
q12	27,53,3	ND	0	.3	.3
q14	36,54,3	4,670	4,670	3,294	1,376
q15	40,64,2	ND	0	0	0
q16a	38,58,6	ND	0	56	56
q16b	38,58,1	ND	0	6.1	6.1
q18a	31,43,1	ND	0	0	0
q18b	31,43,5	ND	0	.1	.1
q20a	45,38,5	ND	0	0	0
q20b	45,38,1	ND	0	0	0
q21	29,54,1	ND	0	1.0	1.0
q22	23,48,1	ND	0	0	0
q23	34,61,1	ND	0	0	0
q24	33,61,1	ND	0	.6	.6
q25	35,62,1	ND	0	0	0
q25b	34,62,5	ND	0	3.0	3.0
q26	43,65,2	ND	0	0	0
q27	42,65,2	ND	0	0	0
q28b	43,66,6	ND	0	.5	.5
q29	37,52,1	1.3	1.3	50	49
q30a	40,54,1	2.3	2.3	65	63
q30b	40,54,3	4	4	203	199
q31	32,55,1	2,710	2,710	3,072	362
q32	38,61,4	ND	0	3.4	3.4
q33	45,40,1	ND	0	0	0
q34	25,42,1	ND	0	0	0
q36	39,45,1	ND	0	.6	.6
q36b	39,45,6	1.6	1.6	7.7	6.1
q37	26,54,5	ND	0	.1	.1
q38a	33,51,6	ND	0	1.7	1.7
q39	51,51,1	ND	0	0	0
q39b	51,50,6	ND	0	0	0
q40	49,50,1	ND	0	0	0
q41	45,53,1	ND	0	11.8	11.8
q41b	45,53,6	190	190	115	75
q42	44,62,4	ND	0	0	0
q42b	44,62,6	ND	0	23	23

Table 2. Measured concentration, calibration target, and simulated concentration for observation wells, Graces Quarters, Aberdeen Proving Ground, Maryland—Continued

Well no. (fig. 4)	Location in model (row, col., layer)	Measured concentration ^A	Calibration target	Simulated concentration	Absolute difference
q43	42,57,1	8	8	3.1	4.9
q44	43,59,1	ND	0	.5	.5
q44b	43,59,6	1,800	1,800	256	1,544
q47	39,51,5	27	27	66	39
q48	33,55,6	1.4	1.4	7.8	6.4
q49	30,56,6	ND	0	.9	.9
q50	33,57,6	ND	0	7.2	7.2
q51	40,64,5	ND	0	1.8	1.8
q52a	50,62,1	ND	0	0	0
q52c	50,62,6	840	840	128	712
q53	48,58,6	21	21	43	22
q55a	58,57,2	ND	0	0	0
q55b	58,57,6	ND	0	0	0
q56	42,47,6	ND	0	11.6	11.6
q57	34,47,5	ND	0	.7	.7
q58	49,65,6	ND	0	52	52
q59	55,64,5	ND	0	8	8
q60	52,57,6	ND	0	0	0

^A: From Dames & Moore, Inc., 1998b, figs. 4–9 and 4–10.

value of 6 meters was used in the calibrated model. The ratio of transverse-horizontal to longitudinal dispersivity was 0.1, and the ratio of transverse-vertical to longitudinal dispersivity was 0.01. Sorption was set so that a retardation factor of 1.3 was attained. The decay rate for 1,1,2,2-tetrachloroethane in the calibrated model was zero. Values of the parameters used in the calibrated ground-water flow and reactive solute-transport models are summarized in table 4.

To determine the effectiveness of the calibration, appropriate calibration targets to represent the measured concentrations (tables 2 and 3) were established. The calibration targets were based on measured concentrations from the direct-push probe investigation conducted during the focused feasibility study in 1995 (Dames & Moore, Inc., 1996), which established the surficial-aquifer plume in three dimensions, and from the 1997 additional ground-water investigation (Dames & Moore, Inc., 1998b), which characterized the plume in the middle aquifer through the installation and sampling of observation wells. Calibration targets in tables 2 and 3 did not always equal the measured concentrations; the reasons for this are described below.

One problem with calibrating the model to concentrations from the two data sets (observation well samples and

direct-push probe samples) is that the data are not necessarily directly comparable. The direct-push probes sampled a small fraction of the aquifer thickness compared to the observation wells at Graces Quarters, which typically have 5- or 10-ft screens. As a result, the concentrations in four direct-push probe samples were many times greater than the highest concentrations in the observation wells. In one case, a concentration of 181,000 µg/L was measured in a direct-push probe sample (dmgp01b, table 3), whereas the concentration in an adjacent observation well was 4,670 µg/L (q14, table 2). In another case, the concentrations in two samples from a direct-push probe that were encompassed by a single model cell differed by an order of magnitude (dmgp14a and dmgp14b, table 3). Because of these results, the calibration targets for the four direct-push probe samples with concentrations greater than 10,000 µg/L were set to what were believed to be more appropriate levels for comparison to the simulations. The calibration target for direct-push probe sample dmgp01b (table 3) was set equal to the concentration at well q14 (table 2). The calibration target for dmgp14b was set to equal the concentration in dmgp14a (table 3). The calibration targets for direct-push probe samples dmgp02a and dmgp21b were set at 5 and 10 percent of their measured concentration, respectively (table 3). This

Table 3. Measured concentration, calibration target, and simulated concentration for direct-push sampling points, Graces Quarters, Aberdeen Proving Ground, Maryland

[No., number; col., column; ND, not detected; measured concentration, calibration target, and simulated concentration are in micrograms of 1,1,2,2-tetrachloroethane per liter of water. Calibration target was based on measured concentration, but in cases where the measured concentration was over 10,000 micrograms per liter, the calibration target was adjusted to a lower value that would better represent the concentration over the thickness of the model layer at that point. Comparison of simulated concentration to calibration target provides a measure of the quality of the calibration. Absolute difference is between the simulated concentration and the calibration target]

Direct-push sampling point no. (fig. 7)	Location in model (row, col., layer)	Measured concentration ^A	Calibration target	Simulated concentration	Absolute difference
dmgp01a	36,54,1	ND	0	112	112
dmgp01b	36,54,3	181,000	4,670	3,454	1,216
dmgp02a	31,56,1	82,000	4,100	1,228	2,872
dmgp02b	31,56,2	ND	0	383	383
dmgp03a	37,58,1	ND	0	3.7	3.7
dmgp04	39,56,4	3,150	3,150	2,211	939
dmgp04a	39,56,1	ND	0	102	102
dmgp04b	39,56,3	3,420	3,420	2,180	1,240
dmgp05a	42,53,1	ND	0	47	47
dmgp05b	42,53,2	ND	0	95	95
dmgp05c	42,53,4	6.7	6.7	183	176
dmgp05d	42,53,6	5.0	5.0	95	90
dmgp06a	35,50,1	ND	0	12	12
dmgp06b	35,50,2	15	15	35	20
dmgp06c	35,50,6	43	43	22	21
dmgp07a	34,52,1	ND	0	15	15
dmgp07b	34,52,3	ND	0	308	308
dmgp08	35,63,1	ND	0	0	0
dmgp09a	41,63,1	ND	0	0	0
dmgp10a	35,56,1	ND	0	83	83
dmgp10b	35,56,2	ND	0	240	240
dmgp11a	35,54,2	ND	0	778	778
dmgp11b	35,54,3	ND	0	858	858
dmgp12a	34,53,1	ND	0	50	50
dmgp12b	34,53,3	ND	0	850	850
dmgp13a	33,53,1	ND	0	428	428
dmgp13b	33,53,2	2,380	2,380	585	1,795
dmgp14a	33,54,3	2,300	2,300	985	1,315
dmgp14b	33,54,3	23,200	2,300	985	1,315
dmgp15a	34,56,1	ND	0	287	287
dmgp16a	34,57,1	ND	0	26	26
dmgp17	34,58,1	ND	0	2.1	2.1
dmgp18	35,59,1	ND	0	.5	.5
dmgp19	35,57,1	ND	0	13	13
dmgp20a	36,56,1	ND	0	50	50
dmgp20b	36,56,2	ND	0	178	178
dmgp21a	36,53,1	ND	0	107	107

Table 3. *Measured concentration, calibration target, and simulated concentration for direct-push sampling points, Graces Quarters, Aberdeen Proving Ground, Maryland—Continued*

Direct-push sampling point no. (fig. 7)	Location in model (row, col., layer)	Measured concentration ^A	Calibration target	Simulated concentration	Absolute difference
dmgp21b	36,53,3	29,800	2,980	1,623	1,357
dmgp22b	31,55,1	3,410	3,410	3,744	334
dmgp23b	30,55,1	ND	0	868	868
dmgp24b	30,56,1	ND	0	167	167
dmgp25b	28,57,1	ND	0	2.9	2.9
dmgp26	33,56,1	ND	0	1,557	1,557
dmgp27a	38,57,1	ND	0	63	63
dmgp27b	38,57,4	ND	0	646	646
dmgp28a	39,58,1	ND	0	8.3	8.3
dmgp28b	39,58,2	ND	0	30	30
dmgp28c	39,58,3	ND	0	49	49
dmgp28e	39,58,5	ND	0	512	512
dmgp29a	37,55,1	ND	0	70	70
dmgp29b	37,55,3	ND	0	445	445
dmgp29c	37,55,4	ND	0	130	130
dmgp30a	42,56,1	ND	0	31	31
dmgp30b	42,56,2	ND	0	120	120
dmgp30c	42,56,3	ND	0	228	228
dmgp31a	38,53,1	ND	0	99	99
dmgp31b	38,53,2	ND	0	536	536
dmgp31c	38,53,3	ND	0	873	873
dmgp32a	36,55,1	ND	0	85	85
dmgp32b	36,55,3	113	113	837	724
dmgp33a	31,53,1	ND	0	269	269
dmgp33b	31,53,2	ND	0	246	246
dmgp34a	33,52,1	ND	0	8.5	8.5
dmgp34b	33,52,2	ND	0	23	23
dmgp35b	31,56,1	ND	0	1,191	1,191
dmgp36b	32,58,1	ND	0	29	29
dmgp37	28,58,1	ND	0	2.0	2.0
dmgp38	30,59,3	ND	0	2.0	2.0
dmgp39b	29,57,1	ND	0	2.5	2.5
dmgp40b	30,58,1	9.0	9.0	10	1
dmgp41	31,58,1	ND	0	11	11
dmgp42a	30,53,1	ND	0	2.6	2.6
dmgp42b	30,53,2	ND	0	3.9	3.9
dmgp43	29,55,1	ND	0	7.4	7.4
dmgp44a	30,53,1	ND	0	2.6	2.6
dmgp44b	30,53,2	ND	0	1.7	1.7
dmgp46	33,57,1	ND	0	182	182
dmgp47b	33,58,1	ND	0	3.8	3.8

Table 3. *Measured concentration, calibration target, and simulated concentration for direct-push sampling points, Graces Quarters, Aberdeen Proving Ground, Maryland—Continued*

Direct-push sampling point no. (fig. 7)	Location in model (row, col., layer)	Measured concentration ^A	Calibration target	Simulated concentration	Absolute difference
dmgp48a	40,57,1	ND	0	22	22
dmgp48b	40,57,3	136	136	238	102
dmgp48c	40,57,4	302	302	1,806	1,504
dmgp49a	41,58,2	ND	0	11	11
dmgp49b	41,58,3	ND	0	16	16
dmgp49c	41,58,4	ND	0	284	284
dmgp51a	44,52,1	ND	0	18	18
dmgp51c	44,52,2	ND	0	35	35
dmgp52a	45,54,1	ND	0	6.3	6.3
dmgp52b	45,54,2	ND	0	13	13
dmgp52d	45,54,3	ND	0	23	23
dmgp53a	37,47,1	ND	0	5.6	5.6
dmgp53b	37,47,2	ND	0	21	21
dmgp54a	35,49,1	ND	0	5.1	5.1
dmgp54b	35,49,3	ND	0	25	25
dmgp55a	39,51,3	38	38	109	71
dmgp55b	39,51,1	ND	0	41	41
dmgp56a	39,49,2	ND	0	55	55
dmgp56b	39,49,4	ND	0	80	80
dmgp57a	46,58,1	ND	0	.5	.5
dmgp57b	46,58,2	ND	0	22	22
dmgp58a	44,57,1	ND	0	6.9	6.9
dmgp58b	44,57,2	ND	0	26	26

^A. Dames & Moore, Inc., 1996, Appendix H.

adjustment, while somewhat arbitrary, allowed for the use of these two samples in the evaluation of the quality of the simulations, and seemed to be a more favorable approach to either rejecting the data as outliers or trying to match values that were higher than the concentrations of sources within the model.

Another problem is that the concentrations of contaminants in some of the observation wells that had been sampled more than once tended to fluctuate (Dames & Moore, Inc., 1998a, table 5–23). The direct-push probe sampling was completed 2 years before the installation of most of the observation wells in the middle aquifer, and the direct-push probe sampling points were not permanent. It is therefore unclear whether the concentrations would have remained the same when samples were collected from the wells in the middle aquifer. It was important, however, to include data from both of the studies for several reasons. First, the direct-push probe data were three-dimensional—that is, many of the boreholes were sampled at more than one

depth. This helped determine the vertical component of the plume dimensions. Second, the direct-push probes were closer together than the observation wells. Third, the direct-push probe study provided information on the horizontal extent of the plume in the surficial aquifer, because it established points in all horizontal directions where contaminants were not detected.

A final problem with assigning calibration targets for each of the direct-push probe samples and observation wells was deciding on a value to assign to samples where contaminants were not detected. The detection limit for 1,1,2,2-tetrachloroethane in the direct-push probe samples was 2.5 µg/L (Dames & Moore, Inc., 1996, table 3–1). The detection limit for 1,1,2,2-tetrachloroethane during the additional ground-water investigation was 1.5 µg/L (Dames & Moore, Inc., 1998b, table 4–6). For simplicity, the calibration target for non-detects in tables 2 and 3 was set at zero.

Table 4. *Values of parameters used in the calibrated ground-water flow and solute-transport models at Graces Quarters, Aberdeen Proving Ground, Maryland*

Parameter	Value or range of values	Units of measurement ^A
Horizontal hydraulic conductivity	0.000006 to 67	feet per day
Vertical hydraulic conductivity	.0000005 to .67	feet per day
Recharge	0 to 9	inches per year
Effective porosity	.25	dimensionless
Longitudinal dispersivity	6	meters
Transverse horizontal dispersivity	.6	meters
Transverse vertical dispersivity	.06	meters
Retardation factor (1,1,2,2-tetrachloroethane)	1.3	dimensionless
Retardation factor (trichloroethene)	1.3	dimensionless
Retardation factor (carbon tetrachloride)	1.8	dimensionless
Retardation factor (chloroform)	1.2	dimensionless
Degradation rate (1,1,2,2-tetrachloroethane)	0	years ⁻¹
Degradation rate (trichloroethene)	0	years ⁻¹
Degradation rate (carbon tetrachloride)	0	years ⁻¹
Degradation rate (chloroform)	0	years ⁻¹
Source flux (1,1,2,2-tetrachloroethane)	20	grams per year
Source flux (trichloroethene)	3.5	grams per year
Source flux (carbon tetrachloride)	5	grams per year
Source flux (chloroform)	5.5	grams per year

^A. English units reported here were converted to SI units for all internal model calculations.

A statistical comparison of the simulated concentrations and the calibration targets presented in tables 2 and 3 produces an RMSE of 482 µg/L, an MAE of 207 µg/L, and an ME of 22 µg/L. The RMSE is about 10 percent of the range of calibration targets, which was 0 to 4,670 µg/L. The statistics provided a quantitative way to compare the values from one run to the next during calibration as a measure of whether a particular change produced beneficial calibration results. The statistics also were useful in determining the sensitivity of the simulations to various changes. The statistics were not, however, the only measure used to compare the quality of individual model runs. Factors such as the shape of the plume, the concentrations at key observation points, and the similarity of the model parameters to measured or inferred hydrologic data were evaluated to determine if any particular run was better than the last.

Sensitivity Analysis The sensitivity of the solute-transport model (RT3D) to changes in eight different input parameters in the ground-water flow and solute-transport models was determined by varying these parameters above and below the values obtained during a preliminary model calibration. These analyses provided an indication of the extent to which the solute-transport simulations are sensitive

to these inputs, and therefore helped with the final calibration and with the assessment of uncertainty. Each of the parameters, with the exception of recharge and porosity, was varied globally from one-tenth to 10 times the calibrated value. Recharge and porosity were varied from about one-half to twice their calibrated values. The input parameters to the ground-water flow model (MODFLOW) were horizontal hydraulic conductivity, recharge from precipitation, and leakance between model layers. The input parameters to the solute-transport model were the dissolved concentration at the sources, the first-order decay rate, the retardation for 1,1,2,2-tetrachloroethane, and the porosity and dispersivity of the porous medium. The sensitivity analyses were based on the 40-year solute-transport simulation. For the ground-water flow model input parameters, the new model-calculated steady-state flow field was input to the solute-transport model, and a 40-year simulation was run. The global RMSE for 1,1,2,2-tetrachloroethane for the sensitivity simulations was compared to the RMSE from the preliminary calibration. The results, which are shown in figures 12 through 14, are plotted as percent increase above the global RMSE for 1,1,2,2-tetrachloroethane in the preliminary calibration.

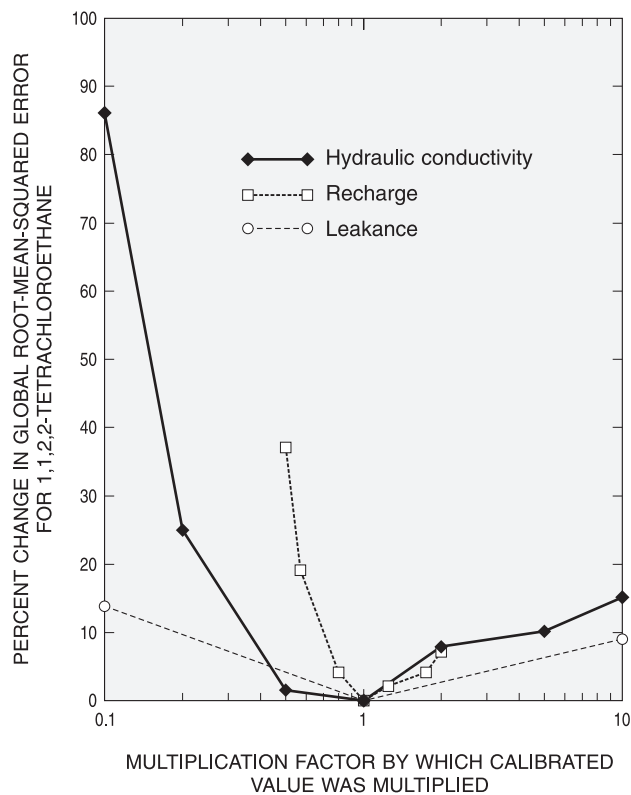


Figure 12. Sensitivity of the preliminary plume calibration to changes in recharge rate, hydraulic conductivity, and leakance.

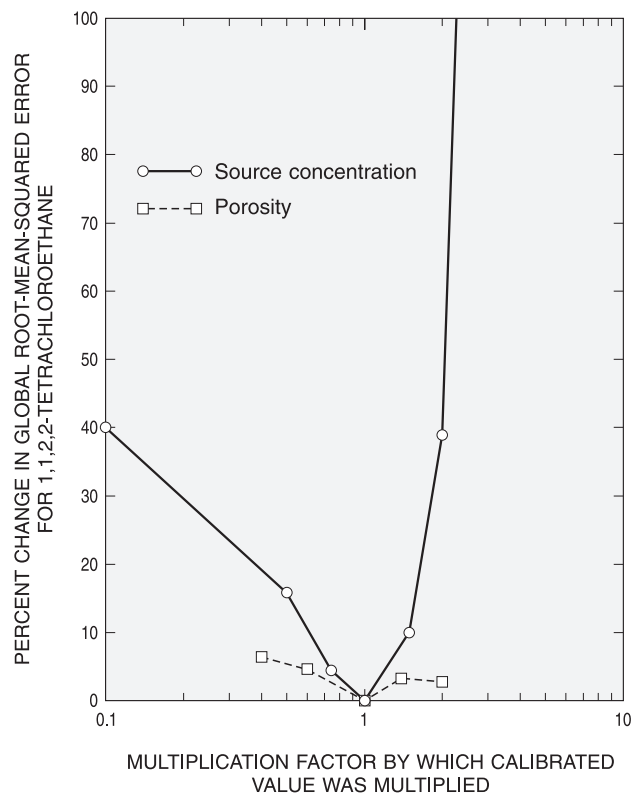


Figure 13. Sensitivity of the preliminary plume calibration to changes in source concentration and porosity.

The results of the analyses for the ground-water flow model input parameters (fig. 12) indicate that the solute-transport model is most sensitive to a global decrease of recharge and horizontal hydraulic conductivity. Decreasing the horizontal hydraulic conductivity by an order of magnitude resulted in an 86-percent RMSE increase; however, a ten-fold increase in the conductivity only changed the RMSE by 15 percent. Similarly, a reduction in recharge by one-half resulted in about a 38-percent change, whereas doubling the recharge only resulted in an 8-percent change. Increasing or decreasing leakance by an order of magnitude resulted in a small change of about 9 to 13 percent.

The transport flow model is most sensitive to the characterization of the source of the dissolved 1,1,2,2-tetrachloroethane as shown in figure 13. An increase of slightly greater than twice the concentration of the 1,1,2,2-tetrachloroethane entering into the dissolved phase from the source resulted in a 100-percent increase in the RMSE. Results of sensitivity analyses indicated that the effect of changing the flux rate at which the 1,1,2,2-tetrachloroethane is entering into the system is identical to that of changing the source concentration. Decreasing either the flux rate or the concentration by an order of magnitude resulted in a change of 40 percent in the RMSE. The effect of increasing or

decreasing porosity over a reasonable range of values (fig. 13) resulted in a minimal change in the RMSE.

The effect of varying either the half-life or retardation of 1,1,2,2-tetrachloroethane, or the dispersivity is shown in figure 14. Retardation analysis was based on varying a retardation function equal to the retardation factor minus one. An increase of ten times the standard values used for the dispersivities results in a relatively moderate change of about 16 percent in the RMSE. All other changes in the three parameters shown in figure 14 result in smaller percent changes to the RMSE. Thus, the overall RMSE of the solute-transport model is neither sensitive to reasonable changes in the inputs for retardation or the half-life of 1,1,2,2-tetrachloroethane, nor the model-calibrated dispersivities (fig. 14).

The fact that the RMSE of the solute-transport model is relatively insensitive to certain parameters indicates that it cannot be used as the sole criterion for evaluating the quality of the calibration. The RMSE appears to be least sensitive to parameters that have a small effect on the higher concentrations in the simulations (which are in areas close to the sources), but have a potentially large effect on the diffuse areas of the plume. For this reason, more qualitative goodness-of-fit measures (such as overall plume shape and

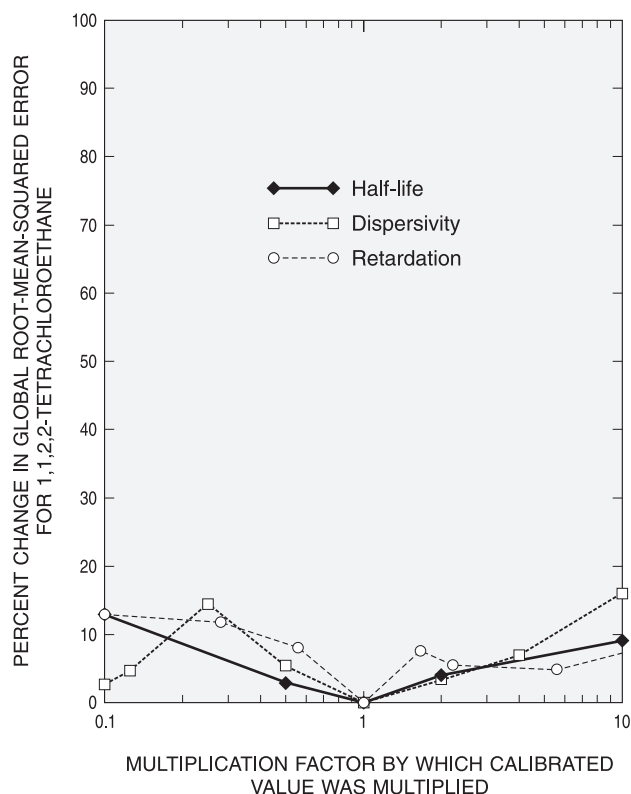


Figure 14. Sensitivity of the preliminary plume calibration to changes in half-life and retardation of 1,1,2,2-tetrachloroethane and dispersivity.

the concentrations at individual sampling points) were also considered during the calibration.

Limitations of the Calibration The calibration of any ground-water flow model or solute-transport model is an inexact procedure that is subject to many limitations. First, there are limits to the amount of data that can be collected and incorporated into the simulations. Second, these simulations tend to be non-unique, which means that there is more than one way to produce essentially the same results. Third, the presence of non-zero error statistics (RMSE, MAE, and ME) in a calibrated model indicates that the calibration targets were not fully achieved.

The limitations in field data at Graces Quarters are believed to be minor, but they could have affected the calibration in several ways. The spatial distribution of wells and direct-push probes provided a three-dimensional coverage of the extent of the contaminant plume, but the complexity of the system means that some areas in the interior of the plume were not sampled. In these areas, the results of the calibration simulations cannot be readily compared to field measurements. Similarly, hydraulic head measurement points were not uniformly distributed within each of the model layers, which makes it difficult to assess the differences between simulated and measured head in

parts of the model area.

Whereas it is difficult to quantify the impacts of the calibration limitations on the use of a specific ground-water flow or solute-transport simulation, some aspects of the Graces Quarters modeling should be noted to help assess the uncertainties. In the ground-water flow model, some of the approximations that might affect the simulations include simulating steady-state flow at a site where seasonal changes occur, not simulating evapotranspiration processes explicitly, not being able to obtain independent water-balance information for the site, and having to interpolate and extrapolate hydraulic parameters over the whole model area. Additional approximations that affect the solute-transport simulations include the locations of contaminant sources and the time when releases commenced, along with the estimates of solute-transport parameters such as dispersivity, sorption, and decay.

Because of the many assumptions and approximations inherent in the model calibration, the results should be used with caution. Simulation results should not be accepted without question, but should be critically evaluated in conjunction with other information about the system and about ground-water flow and solute transport in general. Conversely, the simulation results should not be categorically rejected because of the assumptions and approximations that went into them. The results can be instructive in several ways—for example, if they disagree with expected results, the assumptions and approximations can be re-evaluated to determine whether and why the results should or should not be trusted.

Multi-Species Solute Transport

Calibration of the Graces Quarters solute-transport model was accomplished through the process of matching simulated concentrations of 1,1,2,2-tetrachloroethane to measured concentrations of the chemical at a large number of observation points. The contaminant plume at Graces Quarters, however, does not consist entirely of 1,1,2,2-tetrachloroethane. Several other compounds, including trichloroethene, carbon tetrachloride, and chloroform are present in high concentrations within the same area as the 1,1,2,2-tetrachloroethane. Relatively simple changes were made within the solute-transport model that was calibrated to the 1,1,2,2-tetrachloroethane plume to simulate the transport of the other three chlorinated hydrocarbons mentioned above. Essentially, the only differences between the simulation of 1,1,2,2-tetrachloroethane transport and transport of the other compounds were that (1) the sorption characteristics of each simulated compound were based on their chemical properties relative to 1,1,2,2-tetrachloroethane, and (2) not all of the simulated source locations for 1,1,2,2-tetrachloroethane were used as source locations for the other compounds, depending on the characteristics of the existing plume for each compound. The rationale behind the source characterization for each of the compounds is described on the next page.

Evaluation of Sources and Ambient Degradation of Contaminants Uncertainty exists about the sources of the compounds within the contaminant plume at Graces Quarters. All compounds are highly chlorinated, and all could have been released at Graces Quarters during military activity when it was an active test area. As mentioned earlier, the most likely source of 1,1,2,2-tetrachloroethane was the decontaminating agent known as DANC. It is possible that the trichloroethene in the Graces Quarters contaminant plume was an impurity associated with the 1,1,2,2-tetrachloroethane in DANC. An investigator at another APG site found that trichloroethene contamination was common in the laboratory-grade 1,1,2,2-tetrachloroethane used for microcosm experiments (Michelle Lorah, U.S. Geological Survey, oral commun., 2000). Conversely, trichloroethene is a possible daughter product of the degradation of 1,1,2,2-tetrachloroethane, and the chloroform in the ground water could have resulted from the degradation of carbon tetrachloride (fig. 15). Because the model used at

Graces Quarters is capable of simulating multi-species reactive transport, it can be used to explore different possibilities for the origins of trichloroethene and chloroform in ground water.

The anaerobic degradation pathways of the chlorinated solvents that are abundant in ground water at Graces Quarters are shown in figure 15. Lorah and others (1997, p. 12–15) discuss studies that have examined the environmental degradation of these compounds. Three degradation pathways for 1,1,2,2-tetrachloroethane are believed to be possible—hydrogenolysis (reductive dechlorination) to 1,1,2-trichloroethane, dichloroelimination to the isomers of dichloroethene, and dehydrochlorination to trichloroethene (Lorah and Olsen, 1999, p. 227; Chen and others, 1996, p. 542). The first two degradation pathways are microbially facilitated; the third pathway is abiotic (Lorah and others, 1997, p. 14). The dominant pathway for *in situ* degradation of 1,1,2,2-tetrachloroethane in soil or ground water is largely unknown (Lorah and Olsen, 1999, p. 228).

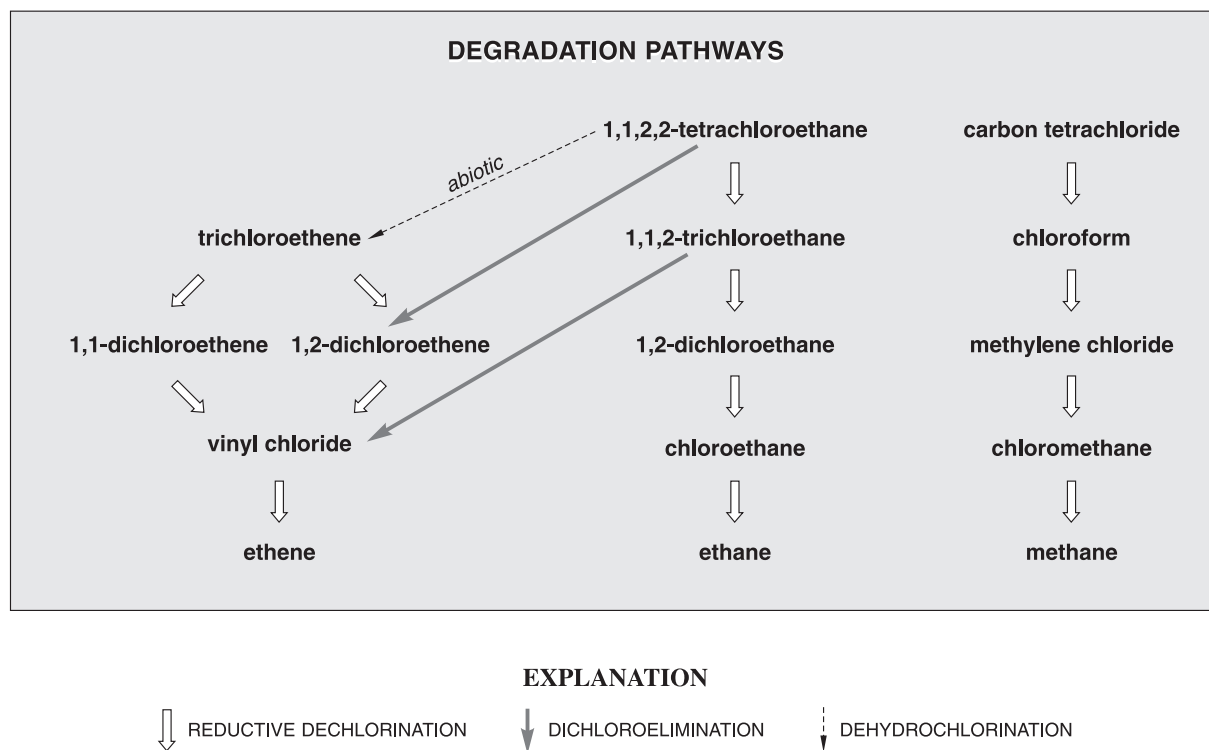


Figure 15. Degradation pathways for 1,1,2,2-tetrachloroethane, trichloroethene, and carbon tetrachloride (modified from Lorah and others, 1997, fig. 5).

In microcosm experiments, Chen and others (1996, p. 546) found that the 1,1,2,2-tetrachloroethane to trichloroethene pathway was minor compared to the formation of 1,2-dichloroethene in tests with a high biomass concentration. In tests with diluted biomass, the pathway was more important. Lorah and Olsen (1999, p. 232) state that the abiotic dehydrochlorination reaction may become a more significant degradation pathway at high concentrations of 1,1,2,2-tetrachloroethane because toxicity effects could possibly reduce the activities of microorganisms. This inhibition of environmental microbial activity by 1,1,2,2-tetrachloroethane is likely—soil sterilization is one of the uses listed for the chemical in the Merck Index (Budavari and others, 1996, p. 1,570).

If 1,1,2,2-tetrachloroethane has undergone degradation through natural attenuation processes within the main part of the plume at Graces Quarters, the most probable degradation pathway is abiotic dehydrochlorination to trichloroethene. Of the daughter products that could be formed from the degradation of 1,1,2,2-tetrachloroethane (fig. 15), the only one that was found in abundance in ground water at the site is trichloroethene, which was detected at many sites up to a concentration of 816 µg/L. None of the daughter products of the microbially facilitated degradation pathways were detected during direct-push probe sampling (Dames & Moore, Inc., 1996, Appendix H), and only isolated detections of 1,1,2-trichloroethane (maximum concentration 18 µg/L), 1,2-dichloroethene (maximum concentration 28 µg/L), and 1,1-dichloroethene (maximum concentration 2.4 µg/L) were detected in observation wells (Dames & Moore, Inc., 1998b, Appendix A). If 1,1,2,2-tetrachloroethane has been degrading at a significant rate, it is likely that one or more of the daughter products shown in figure 15 would build up downgradient of the source, because rapid degradation of all of the daughter products is unlikely in the Graces Quarters aquifers. This indicates that either (1) the primary daughter product of the degradation of 1,1,2,2-tetrachloroethane at Graces Quarters is trichloroethene, or (2) trichloroethene is a parent compound at Graces Quarters, and 1,1,2,2-tetrachloroethane has not degraded rapidly enough to produce significant amounts of daughter products such as 1,1,2-trichloroethane or the dichloroethene isomers prior to the mid-1990s sampling.

Attempts were made using reactive solute-transport modeling to determine which scenario provided the best match to the available data. Throughout much of the calibration process, it was assumed that 1,1,2,2-tetrachloroethane degraded to trichloroethene with a half-life of 27 years, based on the preliminary results of the natural attenuation study (T. Llewellyn, URS Corporation, written commun., 1999). Results from these calibration efforts indicated that the trichloroethene concentrations that were detected in the plume could be explained if the only source of trichloroethene was the degradation of 1,1,2,2-tetrachloroethane. Good results also could be obtained, however, using a mixed source of the two compounds with no natural degradation of either compound.

Further analysis of the contaminant concentration data provided indications that the degradation pathway of 1,1,2,2-tetrachloroethane to trichloroethene was not occurring in the aquifer along the presumed ground-water flow paths between wells. If trichloroethene was not present at the upgradient contaminant source, but was formed by the degradation of 1,1,2,2-tetrachloroethane along a ground-water flow path, the relative proportions of the two chemicals should change as the contaminated water moves downgradient. Near the contaminant source on the upgradient side of a flow path where contaminant concentrations are high, relatively more 1,1,2,2-tetrachloroethane should be present in a sample. Farther away from the source, where contaminant concentrations are lower and degradation has had more time to occur, relatively more trichloroethene should be present in a sample.

The scenario described above was tested with a scatter plot and linear regression (fig. 16) comparing the concentrations of 1,1,2,2-tetrachloroethane and trichloroethene in four samples from the natural attenuation study (T. Llewellyn, URS Corporation, written commun., 1999). The data plot on a straight line, with a correlation coefficient (R^2) of 0.9943. It is apparent from this plot that the relative concentrations of the two chemicals are essentially the same in all of the samples, indicating that trichloroethene probably was present at or near the contaminant source, and that degradation of 1,1,2,2-tetrachloroethane to trichloroethene within the aquifers between these wells is not a significant process.

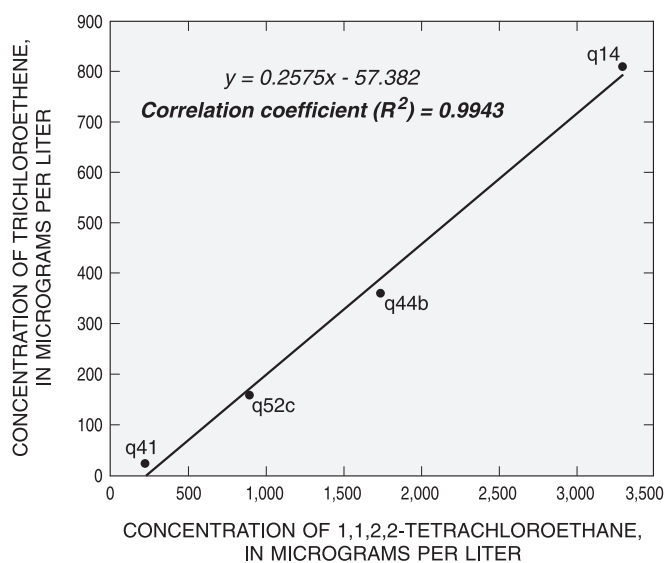


Figure 16. Comparison of 1,1,2,2-tetrachloroethane and trichloroethene concentrations in samples from selected wells, Graces Quarters, Aberdeen Proving Ground, Maryland, spring 1998.

Table 5. Injection rates of chlorinated hydrocarbons for multi-species solute-transport simulations at Graces Quarters, Aberdeen Proving Ground, Maryland

[Injection rate is liters of water per day; concentrations are in grams per liter, and are based on the solubility of each compound in water or on the effective solubility of a hypothetical mix of the compounds in water]

Source location in model (row, column, layer)	Injection rate	Concentration of 1,1,2,2-tetrachloroethane	Concentration of trichloroethene	Concentration of carbon tetrachloride	Concentration of chloroform
31,55,1	0.001	2.61	0.45	0	0
31,56,1	.001	2.61	.45	.785	0
32,55,1	.001	2.61	.45	0	0
33,54,3	.0001	2.61	.45	0	0
36,54,3	.0084	2.61	.45	.71	.82
38,56,3	.01	2.61	.45	.71	.82

Based on the above analysis, it was determined that the best approach for simulating transport of chlorinated hydrocarbons at Graces Quarters was to use mixed contaminant sources and degradation rates of zero for all simulated compounds. It is considered very likely that ambient degradation of contaminants occurs in some parts of the ground-water system, but with the available data, it is extremely difficult to characterize the degradation in a meaningful way. The simpler approach appears to have produced results that are instructive about contaminant transport at Graces Quarters, so the final calibration and the forward simulations were done using degradation rates of zero.

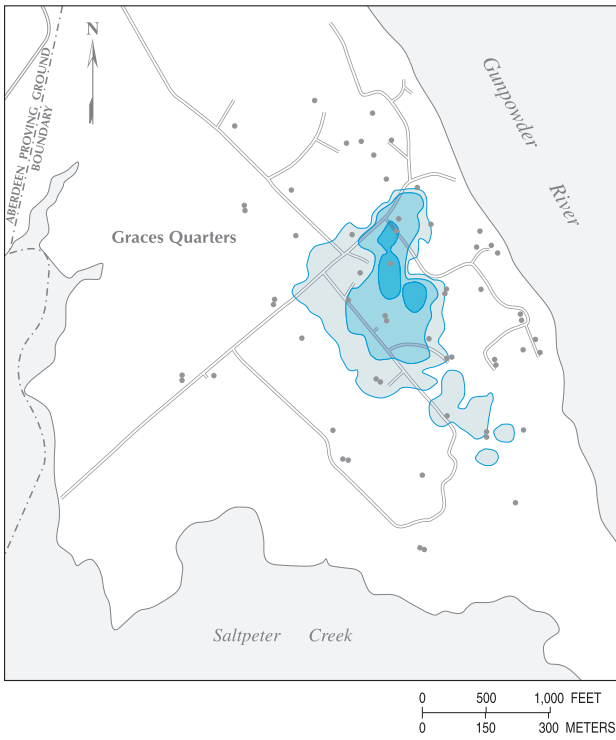
The plume configurations that resulted from the final calibration simulations are shown in figures 17 and 18. Simulated plumes for the four compounds were generated in two separate model runs—one for 1,1,2,2-tetrachloroethane and trichloroethene, and the other for carbon tetrachloride and chloroform. The MODFLOW simulation that generated the head and flow field for solute transport was the same for both of the simulations. In the MODFLOW simulation, small volumes of water were continuously injected at each of the source locations that were set up during the 1,1,2,2-tetrachloroethane calibration efforts. In each of the solute-transport simulations, a mixture of chlorinated hydrocarbons was injected at the source locations (table 5). The concentration of each component of the mixture was based on the effective solubility of the compound in a hypothetical DNAPL mix of the two components in each of the simulations that produced the best calibration results. Essentially, the injection scheme was a way to get an appropriate mass of contaminant into the simulation so that the transport would be realistic. Other approaches to source injection might be equally valid.

Comparison of figures 17 and 18 to earlier figures showing the horizontal extent of the observed plumes in the

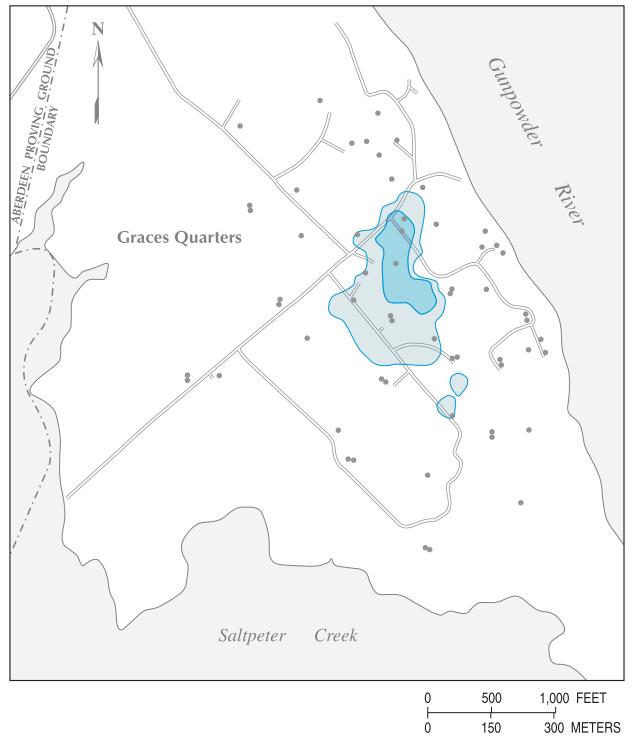
mid-1990s (figs. 8 and 9) provides some indication of the strengths and weaknesses of the solute-transport simulations. One obvious weakness is that the simulated plumes (figs. 17 and 18) are larger than the observed plumes (figs. 8 and 9). This resulted in part from modeling errors—it was extremely difficult to limit the simulated transport in some areas of the plume and extend the transport in other areas of the plume without compromising the available data. Some compromises in the quality of the plume match were necessary because an exact match was impossible. Part of the difference between the observed and simulated plumes, however, might be due to differences in the way different parts of the plumes are represented.

The plumes shown in figure 8 are based on the sampling of direct-push probes during the summer of 1995. Protocol for sampling with direct-push probes was that the probes could not be advanced through any clay unit greater than 2 ft thick (Dames & Moore, Inc., 1996, p. 3–4). This protocol was designed to minimize the potential for cross-contamination of aquifers if DNAPL was present in the subsurface. As a result, some of the sampling locations were terminated prior to reaching the depth at which contamination was present, making the plumes look smaller than actual. The simulated plumes in figure 17 were generated from model layer 3, which is not directly analogous to the parts of the surficial aquifer sampled during the direct-push probe investigation. At the southeastern (downgradient) end of the plumes, layer 3 represents aquifer material that underlies confining-unit material, and was therefore not sampled during the direct-push probe investigation. Wells that were drilled during later investigations of the middle aquifer in the area (Dames & Moore, Inc., 1998b) were screened in the bottom part of the middle aquifer, represented by model layer 6. This means that no data are available to confirm or refute some of the downgradient contamination in the simulation shown in figure 17.

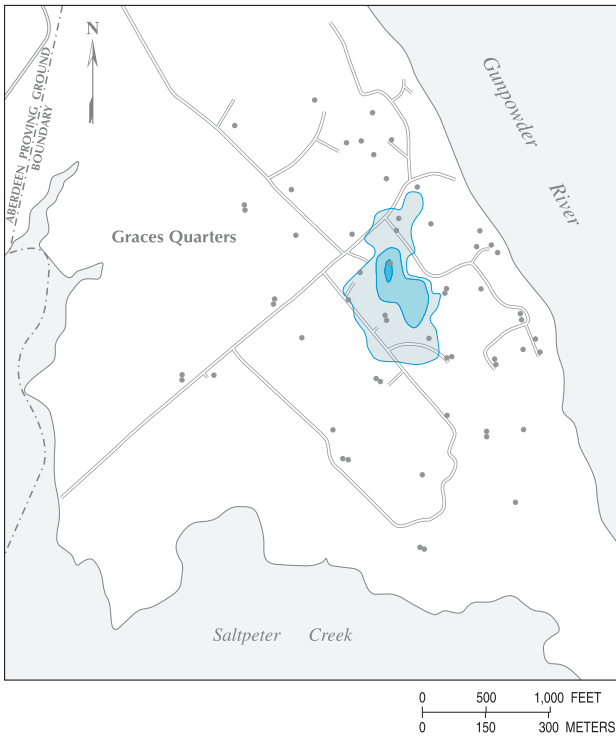
**1,1,2,2-TETRACHLOROETHANE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



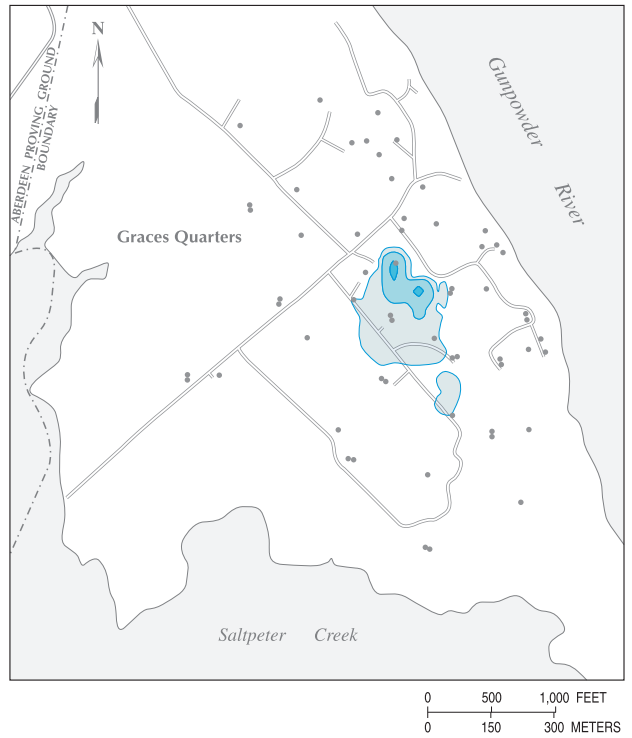
**TRICHLOROETHENE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CARBON TETRACHLORIDE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CHLOROFORM CONCENTRATIONS,
IN MICROGRAMS PER LITER**

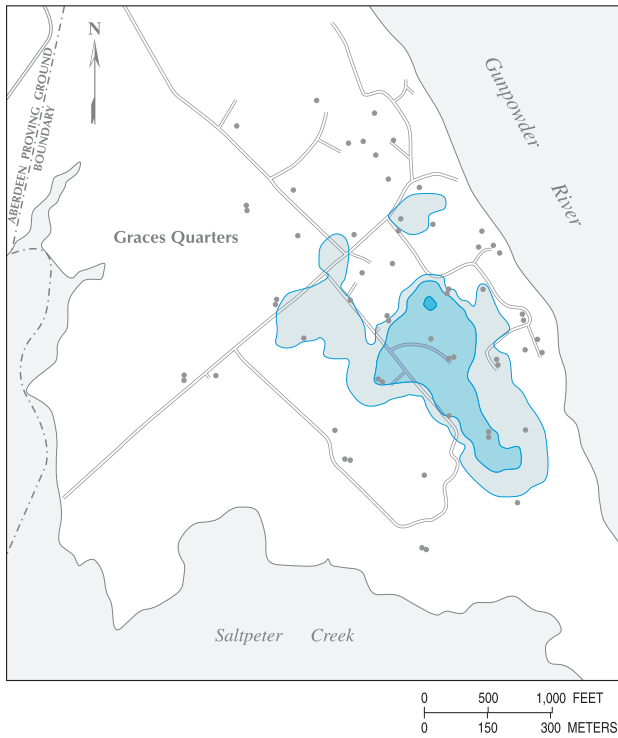


EXPLANATION

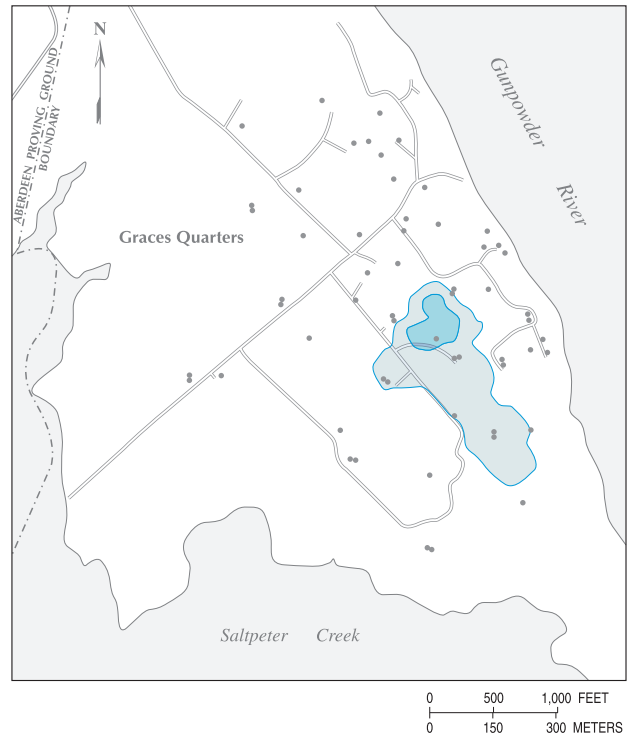


Figure 17. Simulated plumes of 1,1,2,2-tetrachloroethane, trichloroethene, carbon tetrachloride, and chloroform in model layer 3, representing initial conditions in the bottom of the surficial aquifer for forward simulations, Graces Quarters, Aberdeen Proving Ground, Maryland.

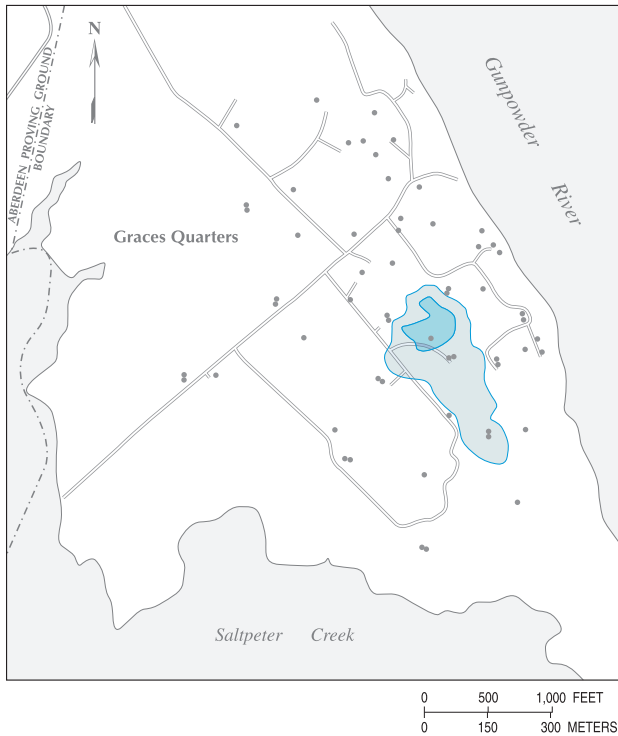
**1,1,2,2-TETRACHLOROETHANE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



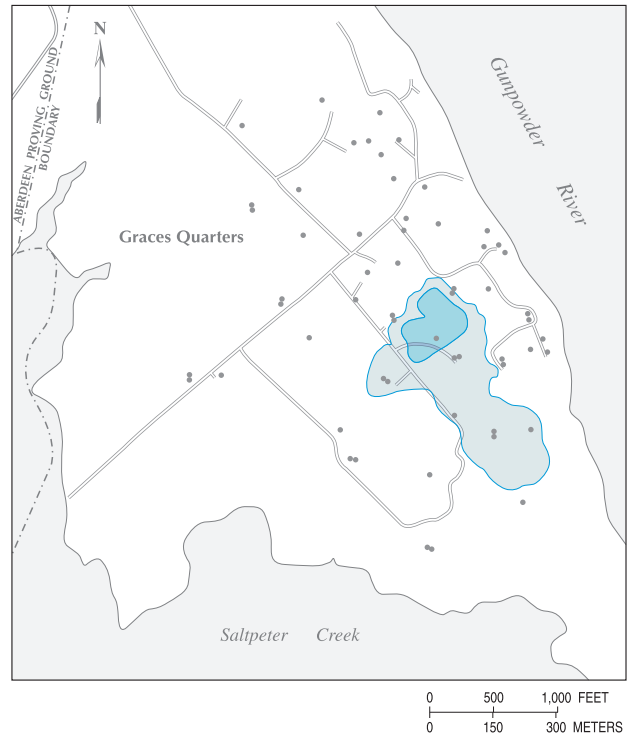
**TRICHLOROETHENE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CARBON TETRACHLORIDE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CHLOROFORM CONCENTRATIONS,
IN MICROGRAMS PER LITER**



EXPLANATION



Figure 18. Simulated plumes of 1,1,2,2-tetrachloroethane, trichloroethene, carbon tetrachloride, and chloroform in model layer 6, representing initial conditions in the bottom of the middle aquifer for forward simulations, Graces Quarters, Aberdeen Proving Ground, Maryland.

Other indications of the quality of the simulations are provided by the error statistics for each of the compounds. The error statistics comparing 1,1,2,2-tetrachloroethane to the calibration targets were provided earlier (RMSE = 482, MAE = 207, and ME = 22 µg/L). The error statistics comparing simulated concentrations of trichloroethene with the measured concentrations (calibration targets in this case were the same as measured concentrations) were as follows: RMSE = 119, MAE = 46, ME = 13 µg/L. The highest measured concentration for trichloroethene was 1,560 µg/L, so the RMSE was less than 8 percent of the concentration range. This compares favorably with the overall error statistics for 1,1,2,2-tetrachloroethane in the same simulation, in which the RMSE was 10 percent of the range of calibration targets. The error statistics for carbon tetrachloride (RMSE = 215, MAE = 55, and ME = -10 µg/L) and chloroform (RMSE = 202, MAE = 45, and ME = 5 µg/L) compare favorably to the range of measured concentrations. The maximum measured concentration for carbon tetrachloride was 2,800 µg/L (Dames & Moore, Inc., 1996, Appendix H); for chloroform, the maximum measured concentration was 3,070 µg/L (Dames & Moore, Inc., 1996, Appendix H).

As with 1,1,2,2-tetrachloroethane, there was some indication that carbon tetrachloride was undergoing degradation to chloroform in the aquifers underlying Graces Quarters. The degradation of carbon tetrachloride can be complex, but under anaerobic conditions, carbon tetrachloride readily undergoes reductive dechlorination (fig. 15) to produce chloroform and methylene chloride (Hashsham and others, 1995, p. 2,856). Carbon tetrachloride has been shown to degrade biologically under denitrifying, sulfate-reducing, and methanogenic conditions (Chiu and Reinhard, 1995, p. 595). Unfortunately, this degradation pathway does not result in the formation of innocuous products in anaerobic systems. Methylene chloride is toxic, and reductive dechlorination of methylene chloride to chloromethane and methane is not extensive enough or fast enough to be useful for remediation (Hashsham and others, 1995, p. 2,856).

Although no records of carbon tetrachloride use at Graces Quarters were found, it was detected in many ground-water samples at the site (Dames & Moore, Inc., 1996, 1998a, 1998b). The chloroform in ground-water samples at Graces Quarters might have resulted from the degradation of carbon tetrachloride, or from its use as a solvent or agent simulant during military testing. No use of chloroform was documented at Graces Quarters, but the compound was mixed with dye and used to simulate chemical agent during testing at Carroll Island (Nemeth, 1989, p. 147), so its use at Graces Quarters is possible. Methylene chloride was not known to have been used at Graces Quarters, and it was not detected in samples from direct-push probes (Dames & Moore, Inc., 1996, Appendix H). It was, however, detected sporadically in five wells (at concentrations of up to 220 µg/L) in the 1997 sampling (Dames & Moore, Inc., 1998b, Appendix A). None of the

other daughter products in this degradation sequence (fig. 15) were detected.

Because of the uncertainty of the degradation of carbon tetrachloride and the origin of chloroform in ground water, the reactive solute-transport model was used to determine if degradation of carbon tetrachloride could adequately explain the chloroform in the ground-water system. Point sources of carbon tetrachloride were set up in the same locations as the sources of 1,1,2,2-tetrachloroethane. Dispersion was the same as 1,1,2,2-tetrachloroethane, but because the sorption of carbon tetrachloride is greater than that of 1,1,2,2-tetrachloroethane or trichloroethene, the retardation coefficient was increased to 1.8. The rate at which carbon tetrachloride degraded to chloroform, which was based on preliminary results from the Graces Quarters natural attenuation study (T. Llewellyn, URS Corporation written commun., 1999), was set such that the compound had a half-life of about 57 years. The chloroform that was created through the degradation of carbon tetrachloride was allowed to degrade in the simulation to methylene chloride at a rate that resulted in an arbitrarily chosen half-life of 99 years. Sorption for chloroform was set such that the retardation coefficient was 1.2, and dispersion was unchanged from the other simulations. Methylene chloride was given a degradation rate of zero, based on the lack of chloromethane in the system and the presence of anaerobic conditions throughout most of the plume. The results of the simulation showed that the measured concentrations of chloroform could not be adequately explained if the only source of chloroform was the degradation of carbon tetrachloride. Because of this and the apparent lack of degradation of the other chlorinated hydrocarbons at Graces Quarters, it was assumed for simulation purposes that ambient degradation of carbon tetrachloride and chloroform was zero.

Because there is little information regarding the use of carbon tetrachloride and chloroform in the military operations at Graces Quarters, model calibration and information from the literature was used to approximate a reasonable source to use in the simulations. Comparison of the pure-phase solubilities of the chemicals (Schwille, 1988, Appendix I) revealed that the solubility of carbon tetrachloride (785,000 µg/L) was much smaller than that of chloroform (8,200,000 µg/L). To obtain a reasonable match of the measured concentrations of each of the chemicals, the effective solubilities of each of the chemicals were calculated for different mole fractions of a hypothetical DNAPL mix to be injected at the same source areas and injection rates used in the 1,1,2,2-tetrachloroethane calibration runs. The best modeling results were obtained by injecting 100 percent carbon tetrachloride, a hypothetical DNAPL consisting of 90 percent carbon tetrachloride and 10 percent chloroform (calculated using the mole fractions), or none of either chemical into each of the simulated sources (table 5).

Forward Simulations Forward simulations of multi-species solute transport were run to evaluate potential future plume configurations at Graces Quarters. Because of the

uncertainties involved in forward simulations, two relatively simple scenarios were run—the first scenario left the simulated sources in the model, and the second scenario removed them. The quality of the forward simulations is directly dependent on the quality of the assumptions made in the conceptual model, the assumptions required to numerically simulate the conceptual model, and the assumptions about the future hydrologic conditions at the site. Each forward simulation evaluates the potential transport of the four main chlorinated hydrocarbons in ground water at Graces Quarters—1,1,2,2-tetrachloroethane, trichloroethene, carbon tetrachloride, and chloroform. It is important to note that although these contaminants are presented separately, the contaminant plume at Graces Quarters generally is a mixture of these dissolved compounds.

Each of the forward simulations described in the following sections starts with the same set of simulated initial conditions (figs. 17 and 18) and was run for 100 years into the future. The initial conditions are the simulated plumes that represent the observed contaminant plumes in the mid-1990s. The initial conditions were generated using continuous point sources of 1,1,2,2-tetrachloroethane, carbon tetrachloride, and chloroform, with no degradation of the compounds as described earlier. Although the initial conditions do not exactly match the measured concentrations in the field, it was felt that this was the most objective way of starting the forward simulations, because the simulated initial conditions are a result of the way the ground-water system was simulated. Use of measured concentrations to represent the initial conditions might have resulted in transient conditions (such as areas of high concentration that are not connected to sources within the model) that could cause the simulated contaminants in the forward simulations to move in a direction or rate that is inconsistent with the conceptual model.

Solute Transport With No Source Removal—The first forward simulation was one in which none of the sources of contaminants were removed, and the natural or steady-state flow conditions were maintained throughout. This simulation was designed to examine how the contaminant plumes might spread and where the plumes might discharge. To illustrate different aspects of the forward simulations, the 30-year and 100-year time steps for selected model layers are discussed below. The 30-year time step was chosen to represent a typical period of time over which different remedial actions are evaluated during feasibility studies. The time step also is within a reasonable length of time beyond the calibration simulations, because historical records indicate that the initial release of chlorinated hydrocarbons into the ground water at Graces Quarters probably occurred between the early 1950s and 1964, and the initial conditions for the forward simulations represent the plume in the mid-1990s. The 100-year time step was chosen to show conditions on a much longer time scale. This time step is more prone to extrapolation errors, but it can be instructive because it provides inferences about how

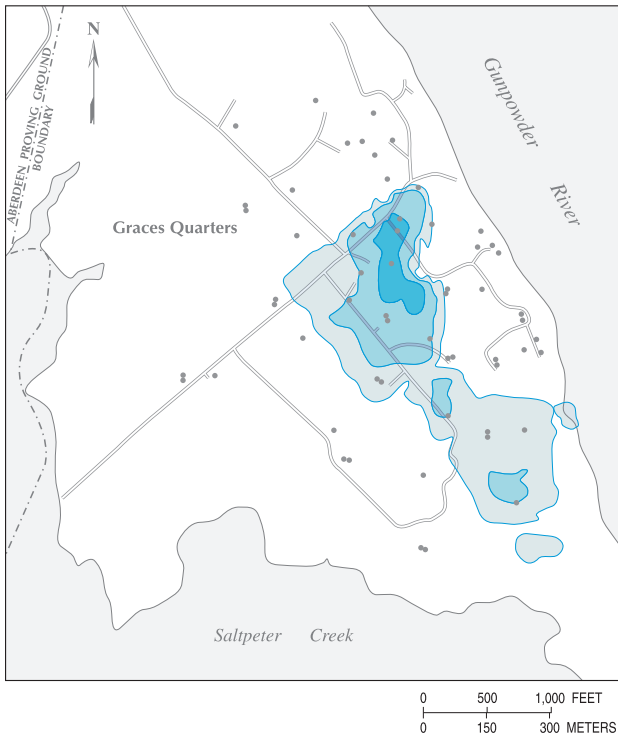
well the simulations conform to the conceptual model, and conversely, the way that the conceptual model is extrapolated beyond the areas that have been investigated at the site.

The results of the 30-year time step of the forward simulations with no source removal are presented in figures 19 and 20. These results indicate that the chlorinated hydrocarbon plumes are likely to continue spreading in the surficial and middle aquifers if no engineered remedial actions are implemented. This result is to be expected, as the simulation does not include contaminant degradation or any other means to stop the spread of contaminants. Comparison of the simulated initial conditions in figure 17 with the simulated future conditions in figure 19 indicates expansion to the southeast for each of the chlorinated hydrocarbon plumes in model layer 3. Within the simulations, this expansion occurs as the contaminants are transported upward from the lower model layers (fig. 20) toward potential discharge zones in the marshes at the southeastern end of the Graces Quarters peninsula.

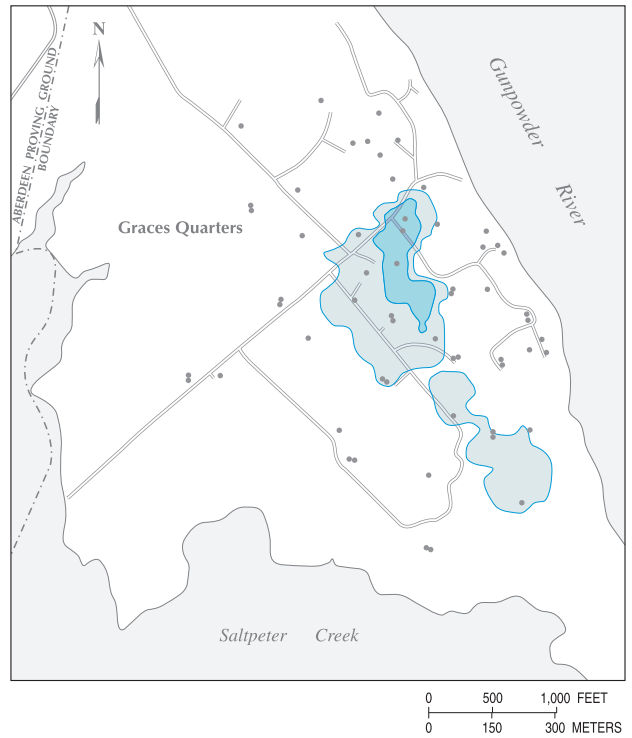
In the simulated middle aquifer (fig. 20), each of the chlorinated hydrocarbon plumes exhibits some expansion to the southeast along the axis of the observed middle aquifer plumes (fig. 9). This simulated transport pathway was based on the conceptual model that the recharge zone for the middle aquifer is in the same area where contaminant sources are present, and the hydraulic conductivity of the aquifer facilitates transport in that direction. The simulated 1,1,2,2-tetrachloroethane plume in figure 20 also shows transport to the west and northwest. This was based on the hydraulic conductivity of the aquifer in that area and a low-level detection of 1,1,2,2-tetrachloroethane (43 µg/L) in the middle aquifer at direct-push-probe sample dmgp06c (see table 3; note that the detection was not included as part of the plume in figure 9, because no observation well exists in that area of the middle aquifer and no sample was collected in 1997).

Results from the 100-year time step of the forward simulation with no source removal are shown for model layer 1 at the top of the surficial aquifer (fig. 21), and for model layer 6 at the bottom of the middle aquifer (fig. 22). Some of the potential discharge zones for the chlorinated hydrocarbons in ground water at Graces Quarters are shown in figure 21, based on the conceptual model used to construct the ground-water flow and solute-transport models for the site. The simulated discharge zones are consistent with the conceptual model, in that they are either in the marshes at the end of the Graces Quarters peninsula, or they are just offshore in the estuaries. Hydraulic head gradients in well clusters near these areas tend to be upward, and the aquifers appear to get thinner near these areas (fig. 3), so it is believed that transport will not continue much beyond the shoreline. The estuaries surrounding Graces Quarters are very large relative to the land area overlying the surficial and middle aquifers, so under current conditions, it is unlikely that sufficient head gradients would develop to allow transport under the estuaries to another land area.

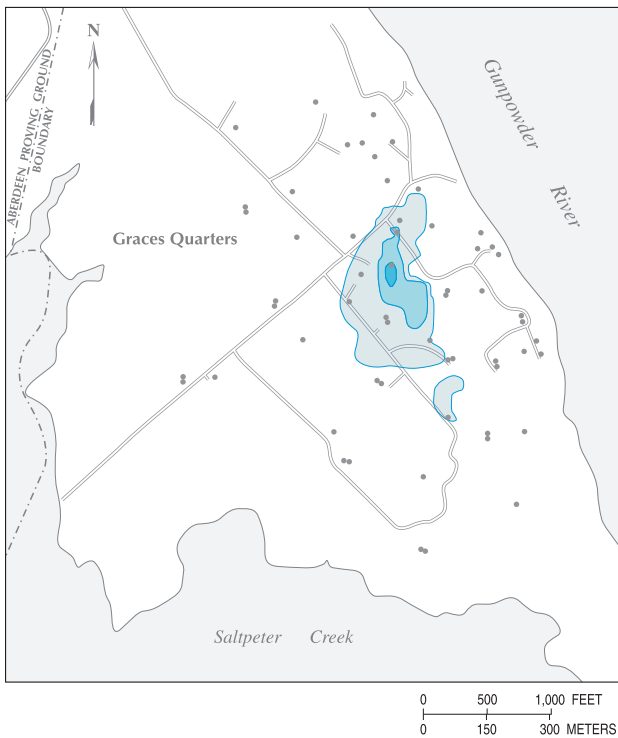
**1,1,2,2-TETRACHLOROETHANE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



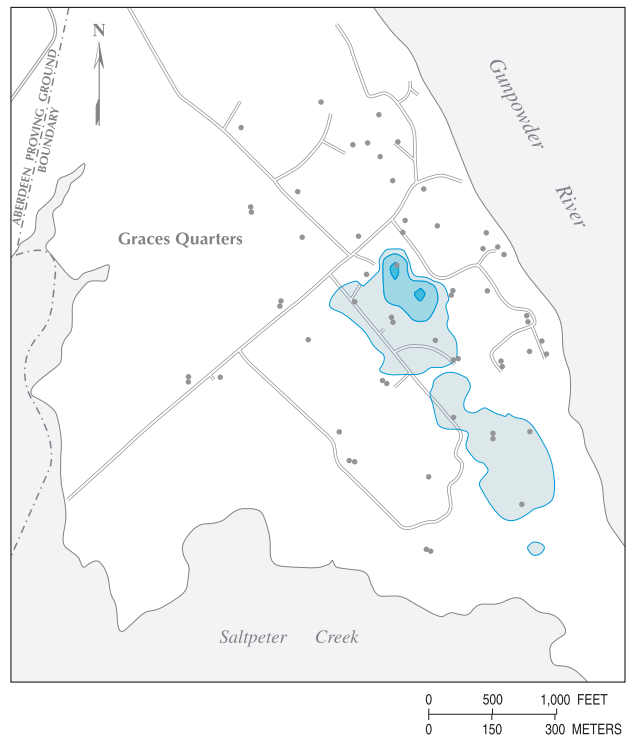
**TRICHLOROETHENE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CARBON TETRACHLORIDE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CHLOROFORM CONCENTRATIONS,
IN MICROGRAMS PER LITER**

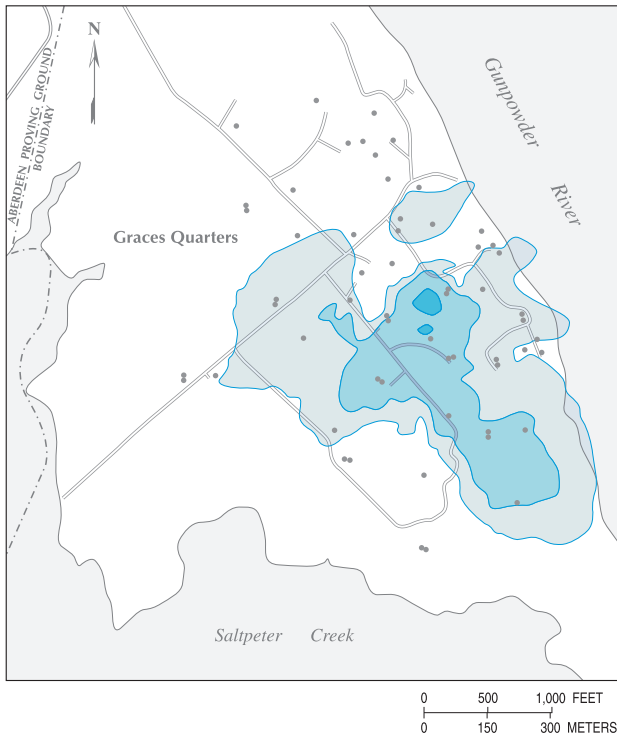


EXPLANATION

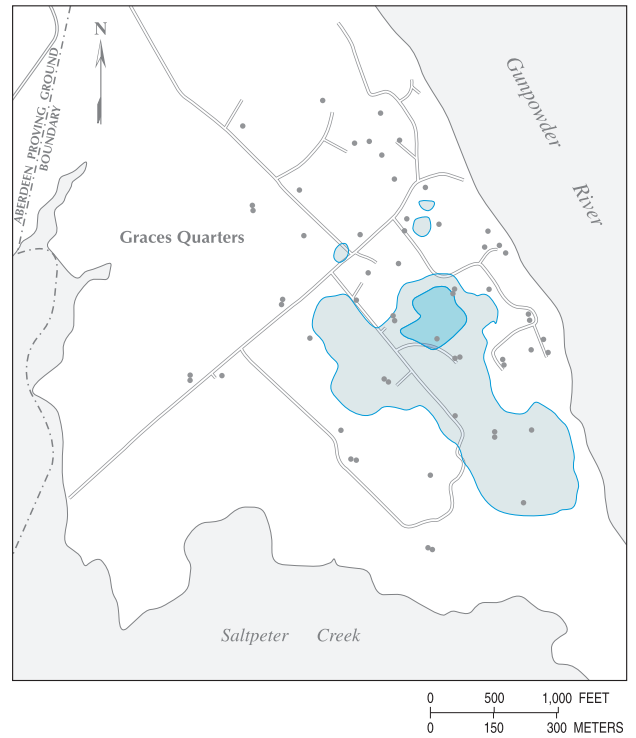


Figure 19. Simulated plumes of 1,1,2,2-tetrachloroethane, trichloroethene, carbon tetrachloride, and chloroform in model layer 3, representing conditions in the bottom of the surficial aquifer after a 30-year forward simulation beyond the mid-1990s distribution of contaminants with no remedial actions, Graces Quarters, Aberdeen Proving Ground, Maryland.

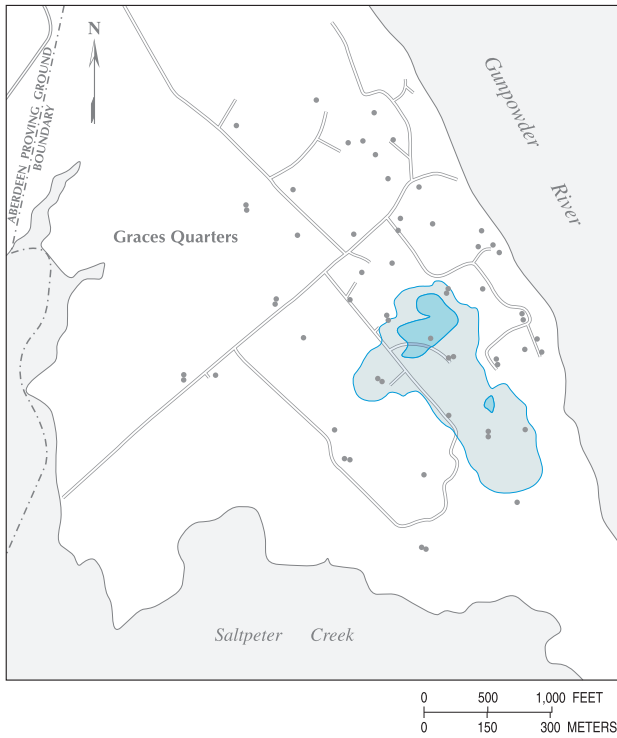
**1,1,2,2-TETRACHLOROETHANE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



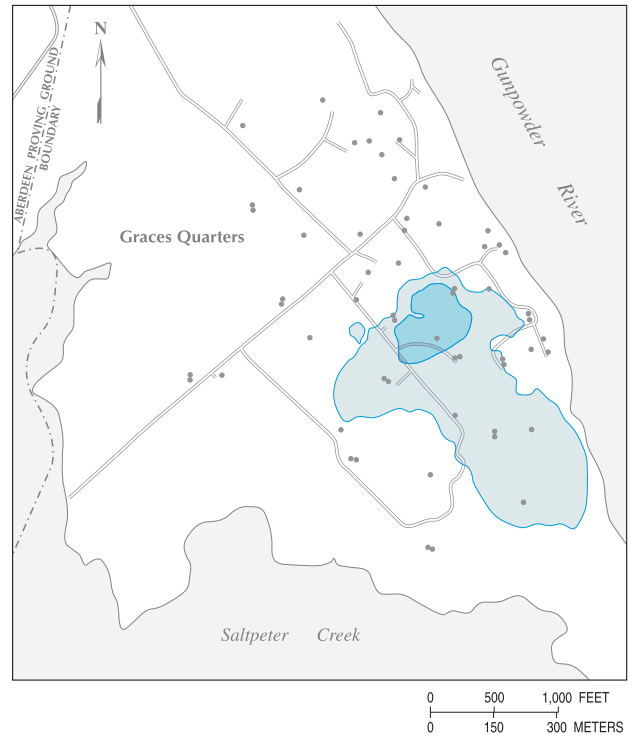
**TRICHLOROETHENE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CARBON TETRACHLORIDE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CHLOROFORM CONCENTRATIONS,
IN MICROGRAMS PER LITER**



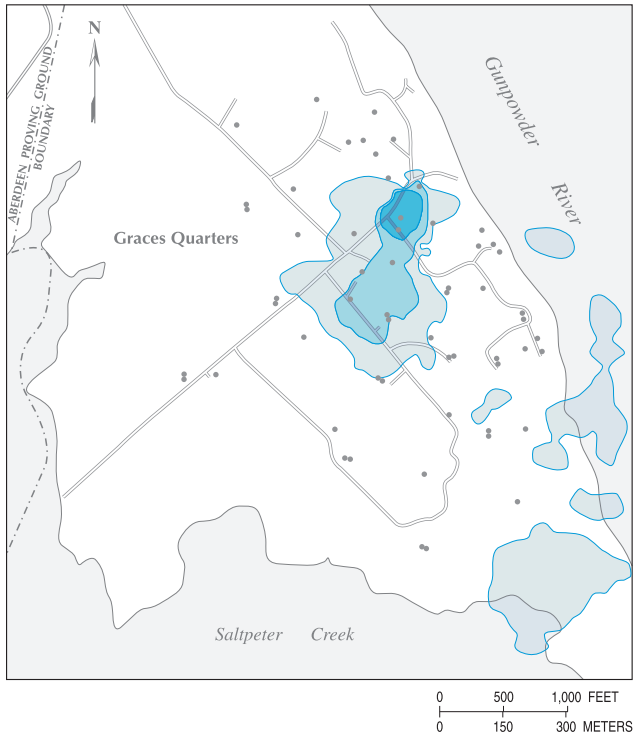
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CONCENTRATION, IN MICROGRAMS PER LITER

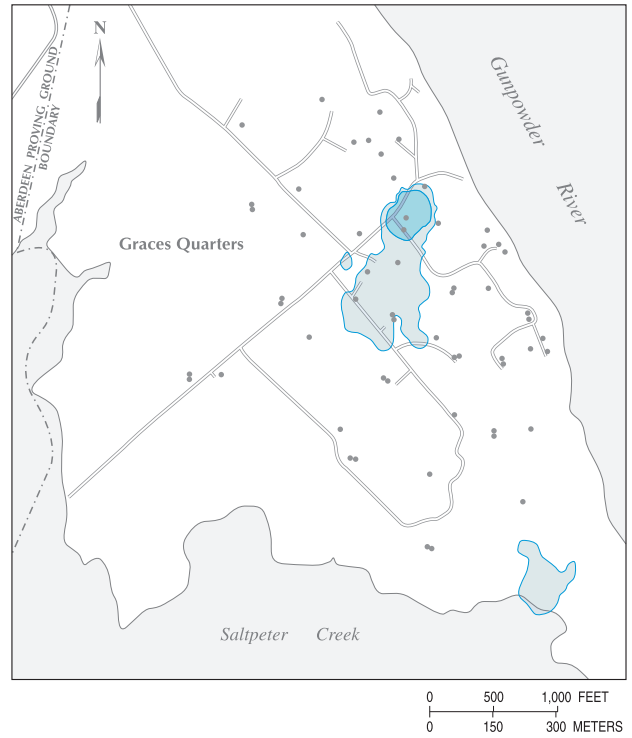


Figure 20. Simulated plumes of 1,1,2,2-tetrachloroethane, trichloroethene, carbon tetrachloride, and chloroform in model layer 6, representing conditions in the bottom of the middle aquifer after a 30-year forward simulation beyond the mid-1990s distribution of contaminants with no remedial actions, Graces Quarters, Aberdeen Proving Ground, Maryland.

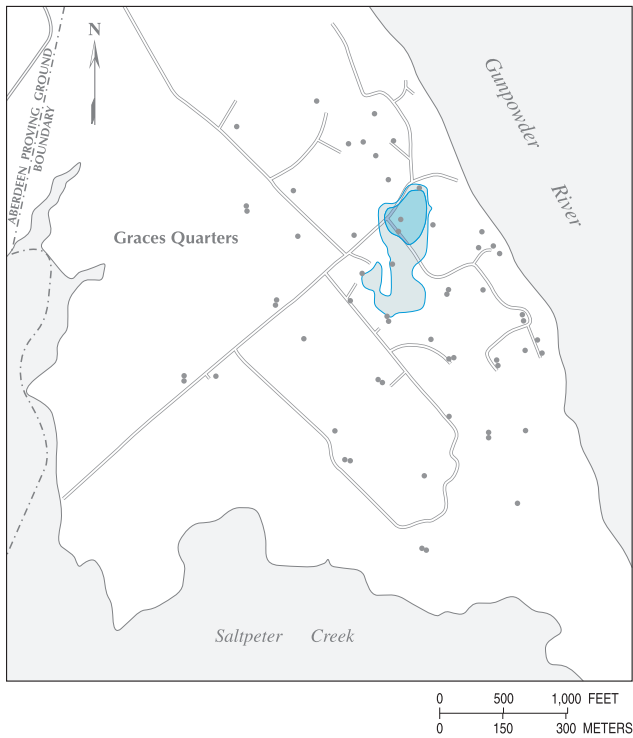
**1,1,2,2-TETRACHLOROETHANE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



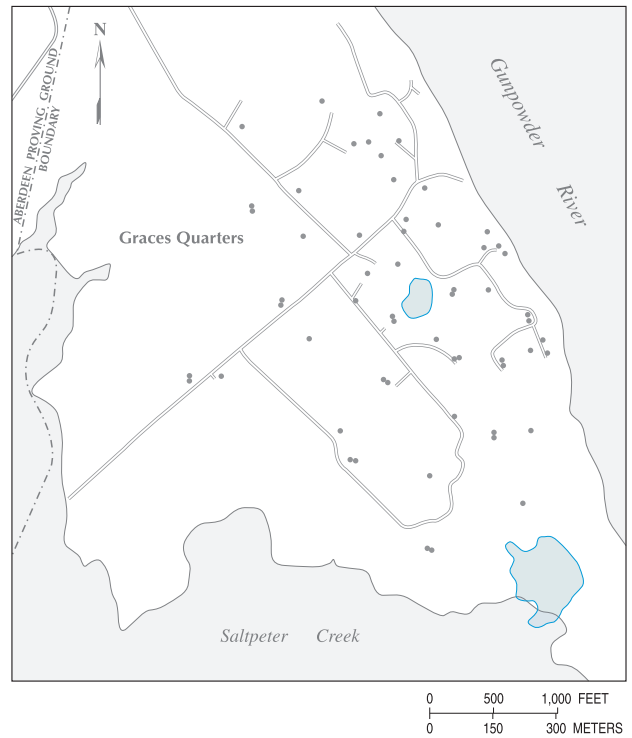
**TRICHLOROETHENE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CARBON TETRACHLORIDE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CHLOROFORM CONCENTRATIONS,
IN MICROGRAMS PER LITER**



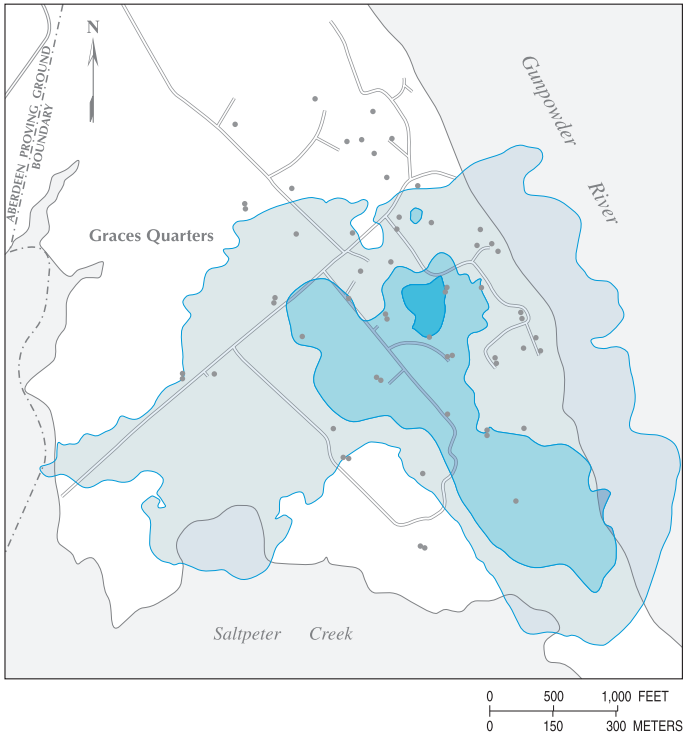
EXPLANATION

CONCENTRATION, IN MICROGRAMS PER LITER

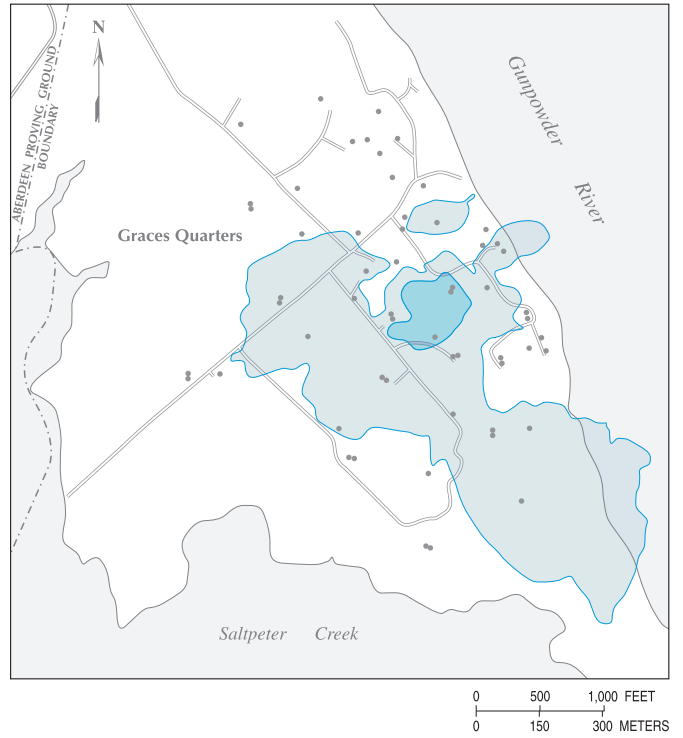


Figure 21. Simulated plumes of 1,1,2,2-tetrachloroethane, trichloroethene, carbon tetrachloride, and chloroform in model layer 1, representing conditions in the top of the surficial aquifer after a 100-year forward simulation beyond the mid-1990s distribution of contaminants with no remedial actions, Graces Quarters, Aberdeen Proving Ground, Maryland.

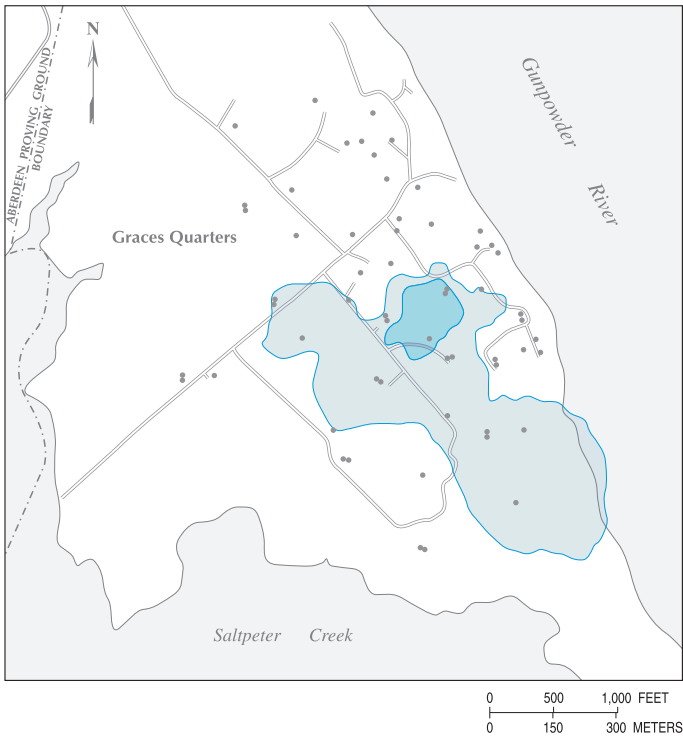
**1,1,2,2-TETRACHLOROETHANE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



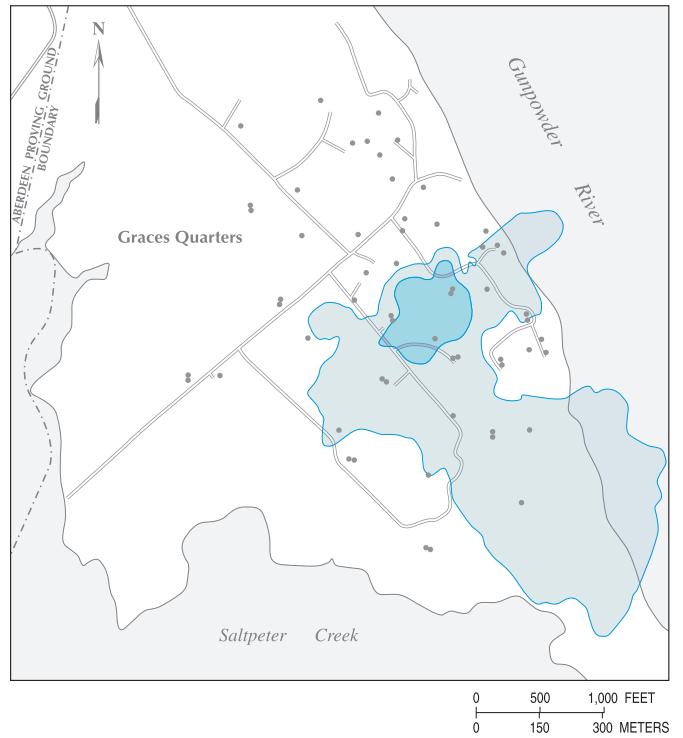
**TRICHLOROETHENE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CARBON TETRACHLORIDE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CHLOROFORM CONCENTRATIONS,
IN MICROGRAMS PER LITER**



EXPLANATION

CONCENTRATION, IN MICROGRAMS PER LITER



Figure 22. Simulated plumes of 1,1,2,2-tetrachloroethane, trichloroethene, carbon tetrachloride, and chloroform in model layer 6, representing conditions in the bottom of the middle aquifer after a 100-year forward simulation beyond the mid-1990s distribution of contaminants with no remedial actions, Graces Quarters, Aberdeen Proving Ground, Maryland.

It should be noted that the discharge of detectable concentrations of chlorinated hydrocarbons to the surface water or marsh areas surrounding Graces Quarters is not likely to occur in reality as it does in the forward simulation (fig. 21). One of the assumptions of the forward simulations is that no degradation of contaminants occurs anywhere in the system. This is not likely to be an accurate assumption, particularly in the marshes, where natural attenuation is expected. Methanogenic conditions, which are conducive to biodegradation of many chlorinated hydrocarbons, are present in some locations at the downgradient end of the Graces Quarters plume within the middle aquifer (T. Llewellyn, URS Corporation, written commun., 1999). Because degradation rates could not be determined in the areas beyond the end of the plume, the degradation rate of zero was used for all simulations, even though degradation is likely.

A scenario of the possible spread of contaminants within the middle aquifer is shown in figure 22. Within model layer 6, the 100-year forward simulation shows the highest concentrations of chlorinated hydrocarbons along the northwest to southeast axis of the plume, with some spreading evident to the southwest as well. These simulations show the contaminants spreading from the central part of the plume toward areas that were simulated with relatively high hydraulic conductivity, which was interpolated and extrapolated onto the model grid based on the results of slug testing in the observation wells screened in the middle aquifer. Much of Graces Quarters is underlain by fairly conductive aquifer material, and figure 22 illustrates the potential for large areas of the aquifer to become contaminated if continuous sources of chlorinated hydrocarbons remain at the site for long periods of time.

Solute Transport With Sources Removed—Solute transport with sources removed was simulated to help determine the level of remedial effort that might be required to restore the aquifer to an uncontaminated state. It is not known whether the aquifer can be restored, or if source removal could be accomplished, but forward simulations with the sources removed might help determine if (a) source removal would be an acceptable remedy for the aquifers at Graces Quarters, or (b) additional ground-water cleanup would be required. Again, these simulations should not be considered as predictive in nature, but they might be instructive about some of the possibilities for transport under this scenario. The forward simulations were set up using the initial conditions as in figures 17 and 18, removing the contaminant sources, and allowing transport to continue forward with no sources.

Forward simulations of the chlorinated hydrocarbon plumes after the sources had been removed for 30 years beyond the initial (mid-1990s) conditions are shown in figures 23 and 24. Comparison of these figures with the scenario where the sources were not removed (figs. 19 and 20) shows a reduction of the concentration of contaminants in the areas nearest the sources, but does not show contamination being completely flushed out of any areas

within the 30-year timeframe. The carbon tetrachloride and chloroform plumes are somewhat smaller in figures 23 and 24 than in figures 19 and 20, but little if any reduction in the size of the 1,1,2,2-tetrachloroethane or trichloroethene plumes is evident. If the assumptions that went into generating the simulated initial plumes are reasonable and ground-water cleanup within 30 years is important, this forward simulation indicates that source removal alone is not likely to be a sufficient remedy.

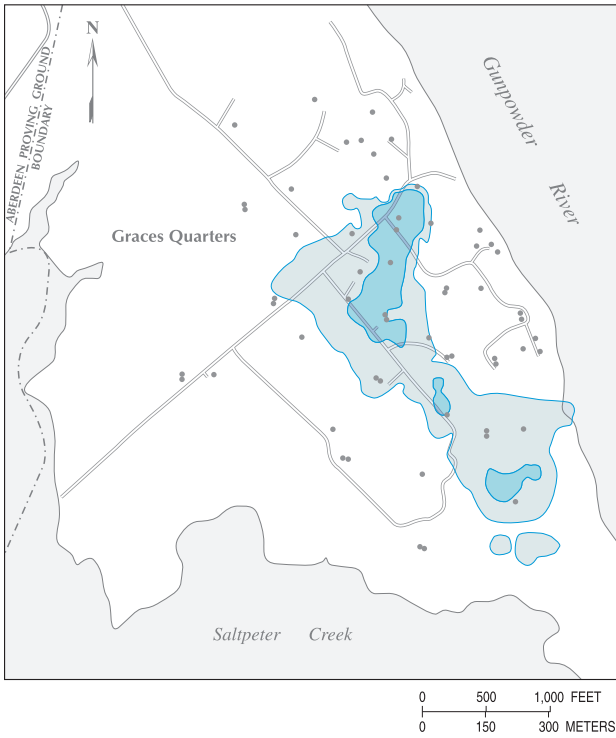
In the 100-year time step of the forward simulation with source removal (figs. 25 and 26), chlorinated hydrocarbons are still present within model layer 6 (representing the middle aquifer) and in isolated areas of layer 1 (representing the top of the surficial aquifer). As before, the assumption of no degradation of the chlorinated hydrocarbons was used, so the only mechanism for removal of contaminants from the aquifer is the flushing of uncontaminated water through the system. The no-degradation assumption may or may not be valid, so the accuracy of the 100-year scenario is questionable. It does, however, illustrate the possibility that source removal alone may not produce a clean aquifer even after 100 years, and that other remediation approaches may be required if ground-water cleanup is expected at Graces Quarters.

Limitations of Forward Simulations—The forward simulations described in previous sections are extrapolations of an imperfect representation of a complex hydrogeologic system. As such, it is important to understand that they are prone to errors, resulting from errors in the conceptual model, in the ground-water flow model, and in the solute-transport model. Only some of these errors can be characterized; others, which result from unforeseen circumstances, cannot. This section is intended to describe some of the possible sources of error in the forward simulations to help the reader assess the results.

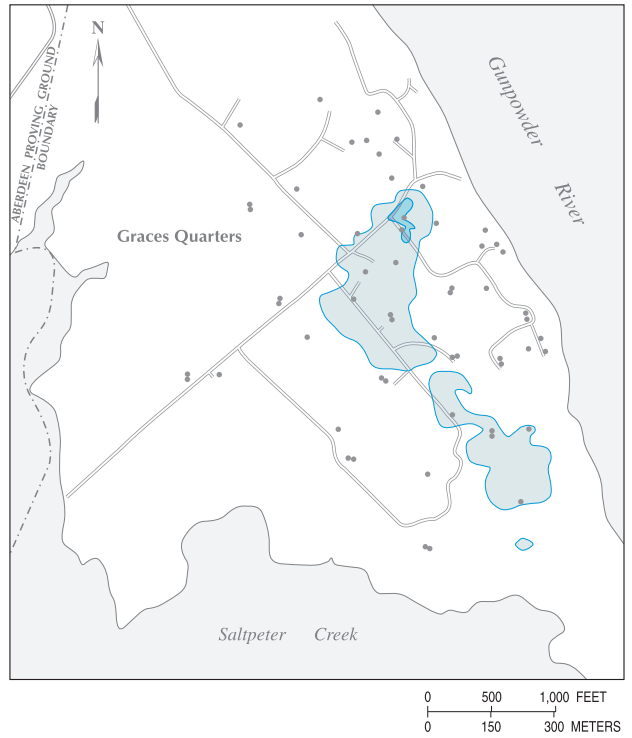
Errors in the conceptual model are somewhat difficult to assess, because the conceptual model is presumed to be the best possible representation of the hydrogeologic system that could be conceived by the investigators. Errors in the Graces Quarters conceptual model have occurred in the past. An earlier ground-water flow model by Tenbus and Fleck (1996) was based on an erroneous conceptual model, which has since been revised (Donnelly and Tenbus, 1998, p. 10–14). The conceptual model that was used for the ground-water flow and solute-transport models in this report resulted from more than 14 years of investigations by several government agencies and hydrogeologic consulting firms, so much of it is likely to be essentially correct. Even the most thoroughly investigated hydrogeologic systems, however, are more complex than can be characterized in a conceptual model. In addition, some important parts of the conceptual model (such as the stratigraphy beneath the estuaries) are based on extremely limited data and could be greatly in error.

Compounding the errors in the conceptual model are errors that are introduced during its incorporation into a ground-water flow model. Ground-water flow simulations

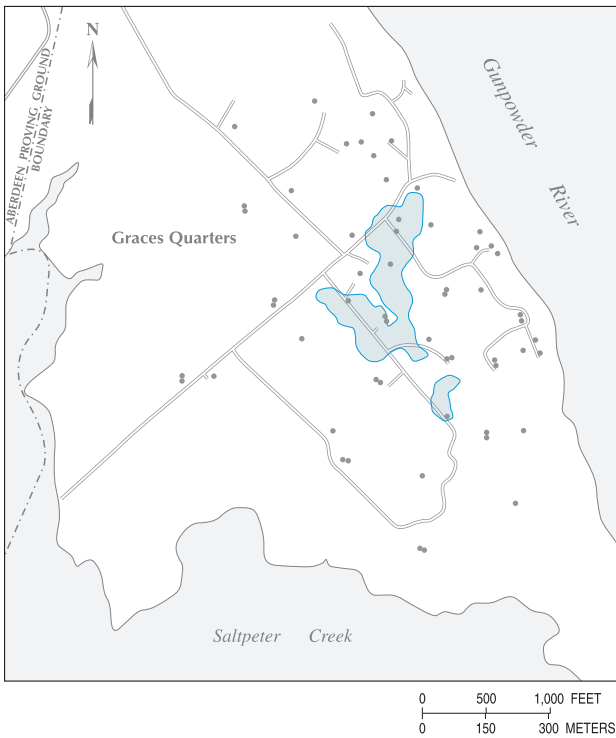
**1,1,2,2-TETRACHLOROETHANE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



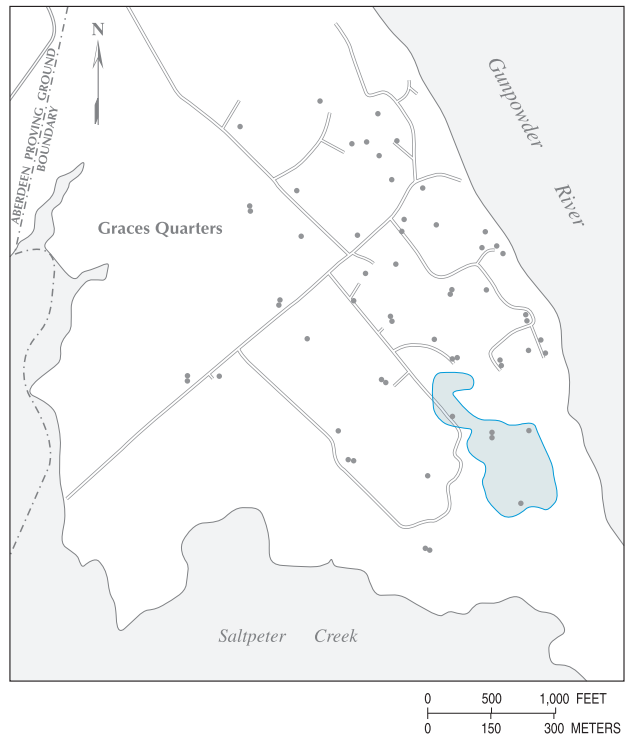
**TRICHLOROETHENE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CARBON TETRACHLORIDE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CHLOROFORM CONCENTRATIONS,
IN MICROGRAMS PER LITER**



EXPLANATION

CONCENTRATION, IN MICROGRAMS PER LITER



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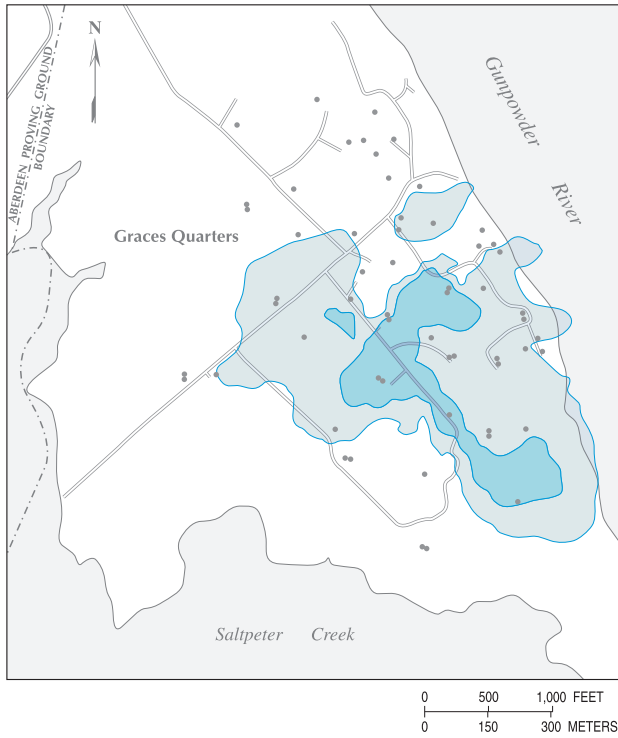


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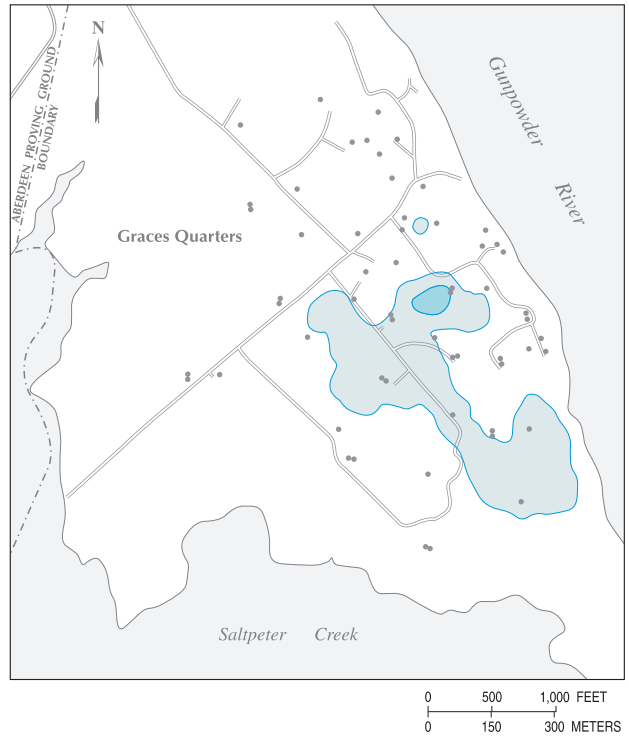
• OBSERVATION WELL

Figure 23. Simulated plumes of 1,1,2,2-tetrachloroethane, trichloroethene, carbon tetrachloride, and chloroform in model layer 3, representing conditions in the bottom of the surficial aquifer after a 30-year forward simulation beyond the mid-1990s distribution of contaminants with source removal, Graces Quarters, Aberdeen Proving Ground, Maryland.

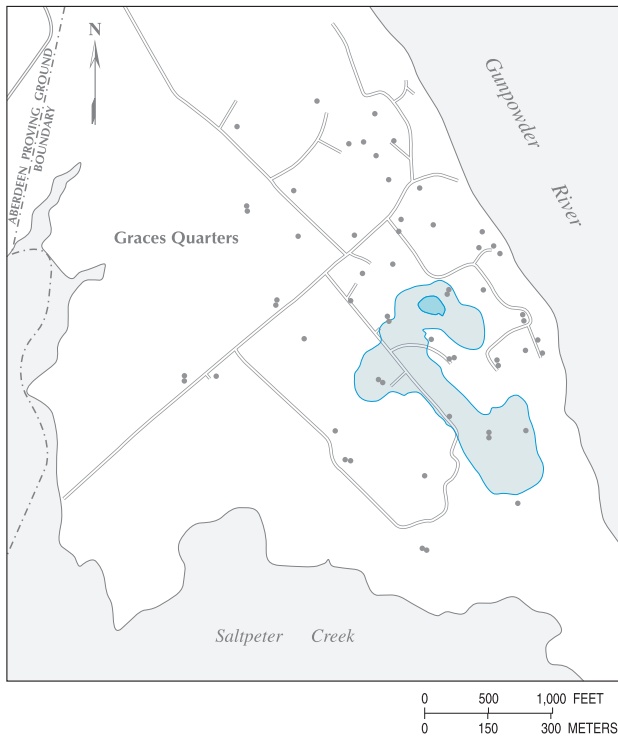
**1,1,2,2-TETRACHLOROETHANE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



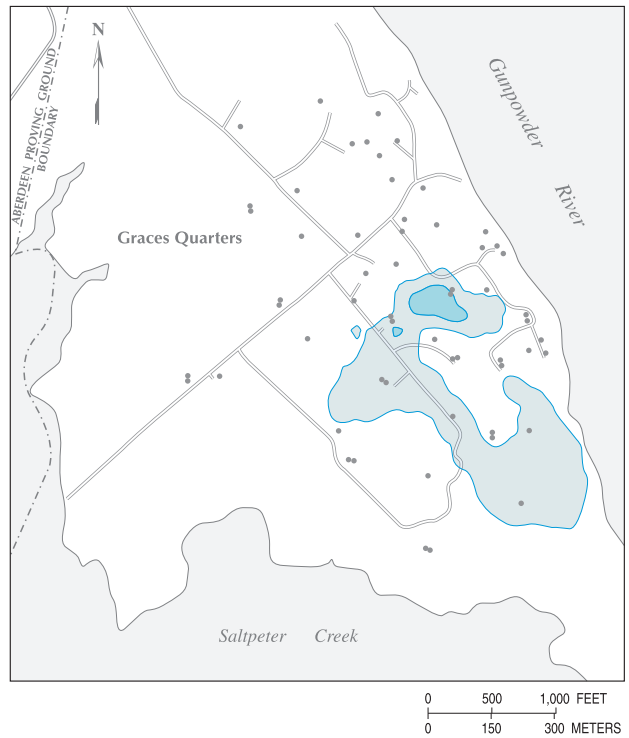
**TRICHLOROETHENE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CARBON TETRACHLORIDE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CHLOROFORM CONCENTRATIONS,
IN MICROGRAMS PER LITER**



EXPLANATION

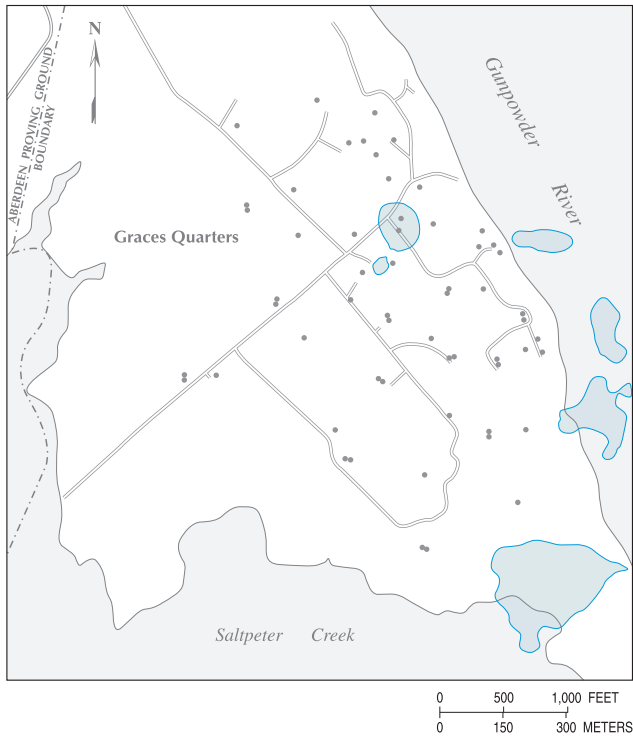
CONCENTRATION, IN MICROGRAMS PER LITER



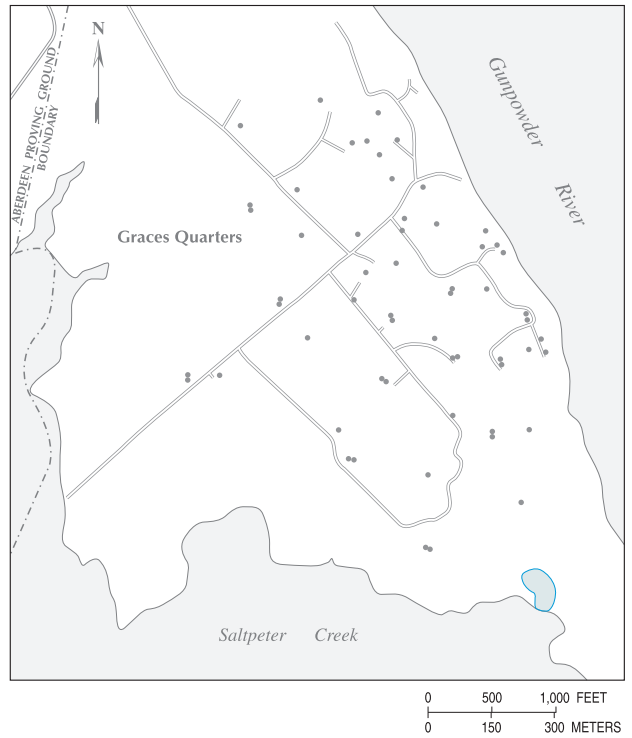
• OBSERVATION WELL

Figure 24. Simulated plumes of 1,1,2,2-tetrachloroethane, trichloroethene, carbon tetrachloride, and chloroform in model layer 6, representing conditions in the bottom of the middle aquifer after a 30-year forward simulation beyond the mid-1990s distribution of contaminants with source removal, Graces Quarters, Aberdeen Proving Ground, Maryland.

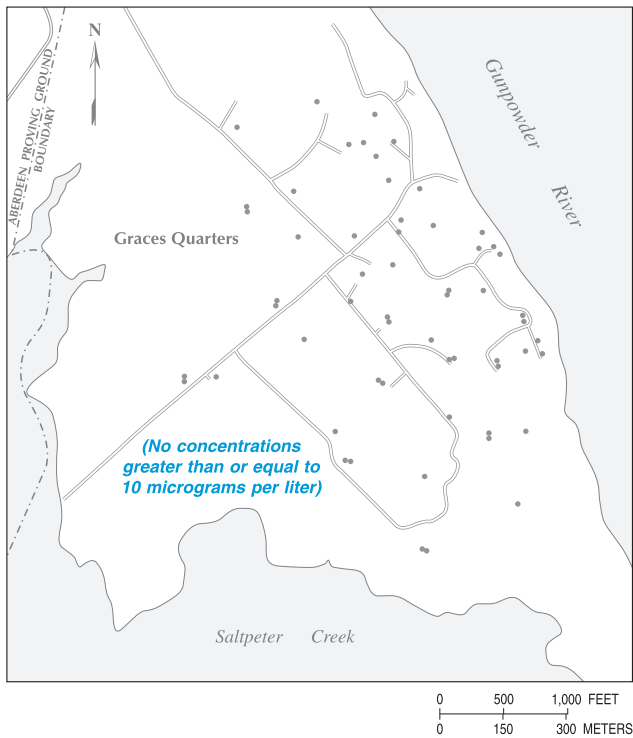
**1,1,2,2-TETRACHLOROETHANE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



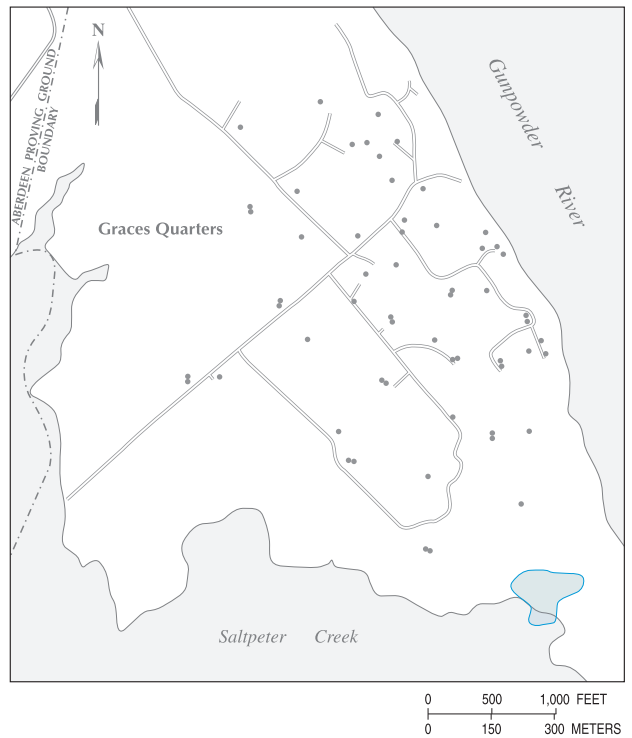
**TRICHLOROETHENE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CARBON TETRACHLORIDE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CHLOROFORM CONCENTRATIONS,
IN MICROGRAMS PER LITER**



EXPLANATION

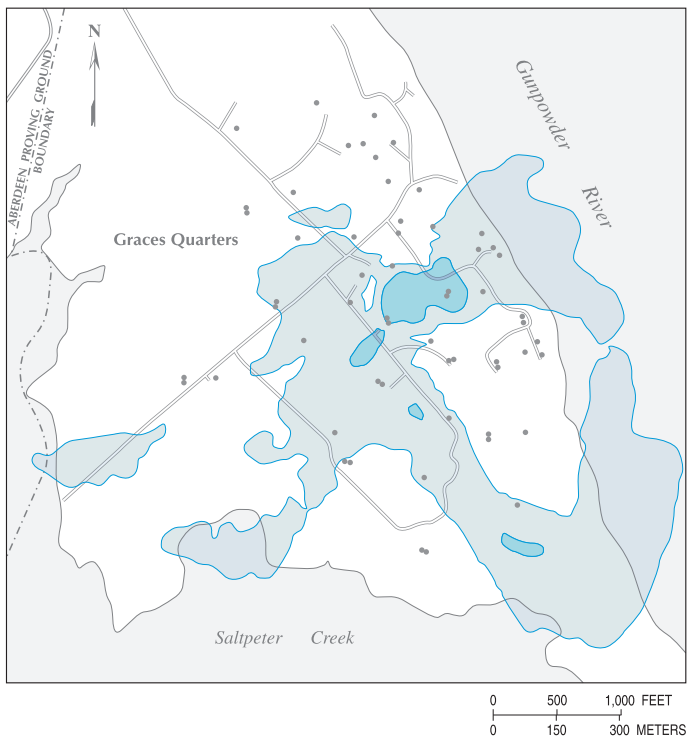
CONCENTRATION, IN MICROGRAMS PER LITER



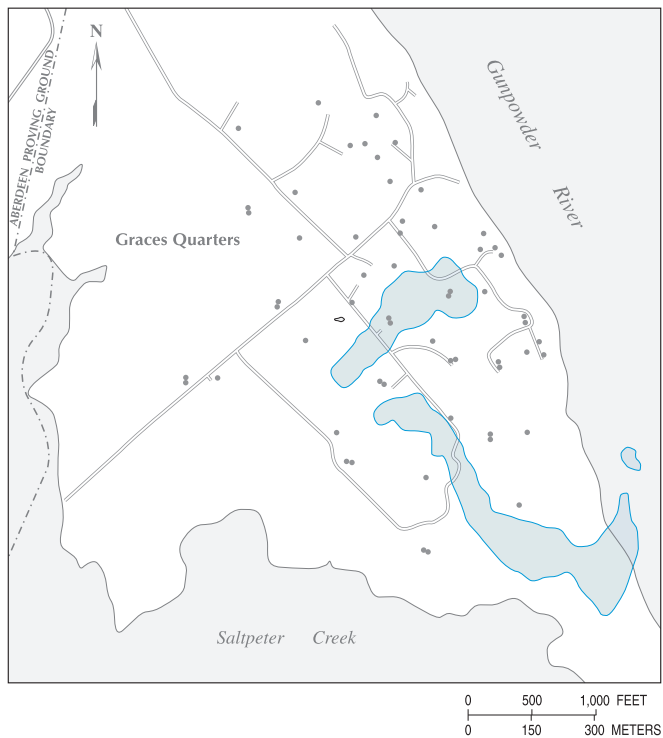
• OBSERVATION WELL

Figure 25. Simulated plumes of 1,1,2,2-tetrachloroethane, trichloroethene, carbon tetrachloride, and chloroform in model layer 1, representing conditions in the top of the surficial aquifer after a 100-year forward simulation beyond the mid-1990s distribution of contaminants with source removal, Graces Quarters, Aberdeen Proving Ground, Maryland.

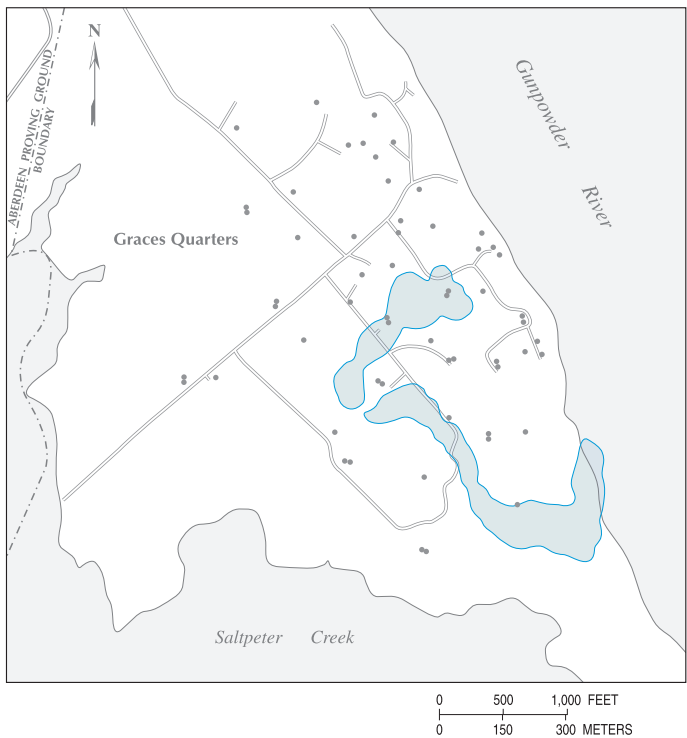
**1,1,2,2-TETRACHLOROETHANE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



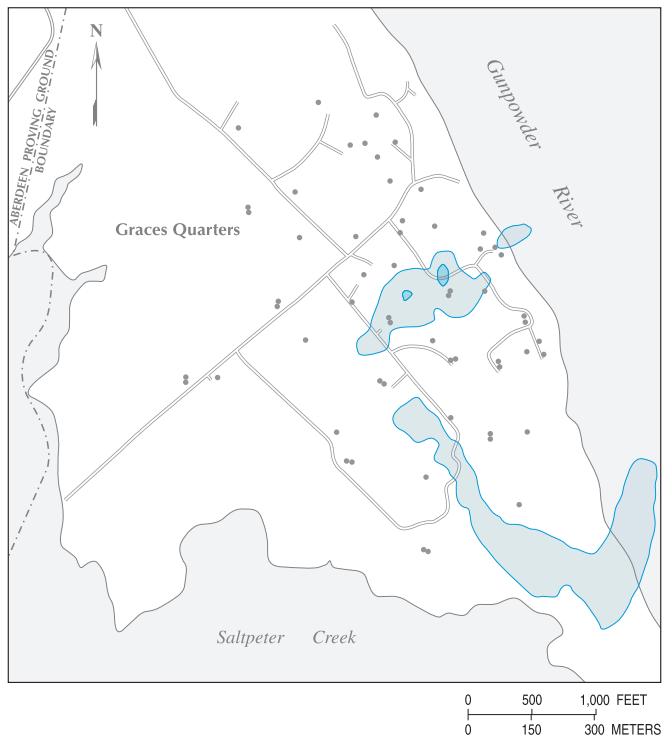
**TRICHLOROETHENE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CARBON TETRACHLORIDE CONCENTRATIONS,
IN MICROGRAMS PER LITER**



**CHLOROFORM CONCENTRATIONS,
IN MICROGRAMS PER LITER**



EXPLANATION

CONCENTRATION, IN MICROGRAMS PER LITER



• OBSERVATION WELL

Figure 26. Simulated plumes of 1,1,2,2-tetrachloroethane, trichloroethene, carbon tetrachloride, and chloroform in model layer 6, representing conditions in the bottom of the middle aquifer after a 100-year forward simulation beyond the mid-1990s distribution of contaminants with source removal, Graces Quarters, Aberdeen Proving Ground, Maryland.

are constructed as simplified versions of hydrogeologic systems, and errors are introduced in the simplification process. Known features of the hydrogeologic system (such as tidal fluctuation in the estuaries, seasonal fluctuation in ground-water head conditions, and evapotranspiration) were ignored to simplify the modeling process. Other features, such as horizontal and vertical hydraulic conductivity, were interpolated and extrapolated onto the model grid from borehole data, and then were adjusted to improve the head calibration. The head calibration produced a non-unique ground-water flow field that did not correctly simulate the direction of solute transport in the initial calibration of the solute-transport simulations.

Errors also are introduced in the solute-transport simulations. Much of the information necessary for solute-transport simulations cannot be precisely determined for the Graces Quarters study area, and must therefore be estimated. The locations of sources and the time of release of chlorinated hydrocarbons into the environment at Graces Quarters can be estimated, but are not precisely known. Solute-transport parameters such as the retardation coefficient and the coefficients of dispersivity are subject to error. In addition, the solute-transport parameters could be spatially variable, and this was not accounted for in the simulations.

Different types of simulation errors would affect the forward simulations in various ways. For example, errors in the conceptual model could potentially be the most serious, because the models were constructed to work in a way that was consistent with the conceptual model of ground-water flow and solute transport at Graces Quarters. The solute-transport simulations do a fairly good job of matching the observed contaminant plume, but if the conceptual model is wrong, the way in which the plume was matched would not mimic the way the observed plume was generated. This means that forward simulations would not accurately represent the future behavior of the observed plume, and the forward simulations would not be useful.

Other potentially serious problems with the forward simulations include the following: (1) contaminant degradation rates and pathways at Graces Quarters could not be characterized over most of the site, especially in the areas beyond the edge of the plume; (2) errors in the coefficients of retardation could affect future transport velocities as well as flushing rates if the sources are successfully removed; and (3) extrapolations in time will magnify any errors that have been made in the simulations. This effect will worsen as the forward simulations are run farther into the future, making the 100-year simulations likely to be very inaccurate. The effect will also be compounded if future land-use or water-use changes occur, which will negate the steady-state conditions that were used for the forward simulations.

Summary and Conclusions

Ground water at Graces Quarters, Aberdeen Proving Ground, Maryland, was contaminated with chlorinated volatile organic compounds as a result of military activity between the late 1940s and 1971. Compounds such as 1,1,2,2-tetrachloroethane, trichloroethene, carbon tetrachloride, and chloroform have been detected at concentrations greater than 1,000 micrograms per liter in the east-central part of Graces Quarters within two hydrogeologic units known as the surficial and middle aquifers. Numerical simulations involving three-dimensional multi-species solute transport were used to assess different concepts about the transport of chlorinated hydrocarbons at the site, and to run forward simulations of solute transport with and without removal of the contaminant sources.

Simulation of ground-water flow within the aquifers and confining units at Graces Quarters involved developing and calibrating a three-dimensional finite-difference ground-water flow model. The model was calibrated to steady-state conditions represented by hydraulic head measured in 58 wells in April 1997. This ground-water flow model was then used as the basis for an initial solute-transport model, which was calibrated to reproduce the configuration of the contaminant plume defined during ground-water investigations in 1995 and 1997. Historical information and field observations and measurements were used to determine approximate source locations and the length of time to run the calibration simulations. For the initial solute-transport calibration runs, a single upgradient point source was used with about 40 years of transport.

Once the initial solute-transport simulations were considered to be satisfactory, additional factors were evaluated to try to improve the simulations. Various configurations of source locations and strengths were evaluated; estimates of dispersivity, sorption, and decay were obtained and adjusted; and hydraulic parameters were refined. Adjustments to these parameters and to source strength and location were used for the final calibration of the solute-transport model to targets that were derived from measured concentrations of 1,1,2,2-tetrachloroethane in more than 150 direct-push probe and observation well sampling locations. Calibration of the solute-transport model resulted in a root-mean-squared error between simulated concentrations and the calibration targets of about 10 percent of the range of calibration targets.

After calibration to the concentrations of 1,1,2,2-tetrachloroethane, relatively simple adjustments were made so that the model could simulate multi-species transport of the other major components of the chlorinated hydrocarbon plume at Graces Quarters. Different options for the sources and degradation of the chlorinated hydrocarbons were evaluated using reactive multi-species solute transport and other methods of data analysis. It was determined that the most practical approach to simulating multi-species transport at Graces Quarters was to use mixtures of contaminants at the sources, and to set the degradation rates of each of the

chlorinated hydrocarbons in the plume to zero. The error statistics for each of the chlorinated hydrocarbons that were simulated using this approach compare favorably with the range of measured concentrations in the observed plume.

Forward simulations of multi-species solute transport were run to evaluate potential future plume configurations at Graces Quarters. Because of the uncertainties involved in forward simulations, the simulations were kept relatively simple, with one scenario maintaining the sources throughout the simulation, and the other scenario removing them at the beginning of the forward run. The simulated plumes from the solute-transport calibration were used as initial conditions, the degradation rates of contaminants were assumed to be zero, and the steady-state ground-water flow conditions from the calibrated model were used throughout.

Each of the forward simulations was run for a period of 100 years beyond the initial conditions that represented the contaminant plume in the mid-1990s. The 30-year and 100-year time steps of the forward simulations were used to illustrate relatively short-term and long-term extrapolations beyond the calibration simulations, so that different aspects of the conceptual model and the way that it was implemented could be shown.

The first forward simulation was run with no source removal. The 30-year time step showed plume growth to the southeast in the model layer that represents the lower part of the surficial aquifer (layer 3), as well as plume growth to the southeast, west, and northwest in the model layer representing the bottom of the middle aquifer (layer 6). The 100-year time step of the forward simulation with no source removal showed potential contaminant discharge zones in the marshes at the end of the Graces Quarters peninsula or just offshore in the estuaries. It also showed continued spreading of contaminants in the middle aquifer. The model simulation does not account for natural attenuation in the marshes or in the methanogenic zones in the middle aquifer at the down-gradient end of the plume, which means that contaminant discharge to the extent shown in the simulations is not likely to occur at Graces Quarters.

The second forward simulation was done with the sources removed to help determine the level of remedial effort that might be required to restore the aquifer to an uncontaminated state. The 30-year time step of this forward simulation indicates a reduction of the concentration of contaminants in the areas near the sources when compared to the simulation where the sources were not removed. It does not, however, indicate that if the modeling assumptions are reasonable, ground-water cleanup within 30 years would occur with source removal alone. The results of the 100-year time step, which are not very likely to be accurate, indicate that source removal alone may not even be effective for cleaning up the ground water within that timeframe.

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