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Comparison of Vapor Concentrations of Volatile Organic Compounds with Ground-Water Concentrations of Selected Contaminants in Sediments Beneath the Sudbury River, Ashland, Massachusetts, 2000

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CONVERSION FACTORS AND ABBREVIATIONS

CONVERSION FACTORS

Multiply	By	To obtain
acre	4,047	square meter
foot (ft)	.3048	meter
inch (in.)	2.54	centimeter
mile (mi)	1.609	kilometer
mil	.0254	millimeter

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

°F=1.8 °C+32

ABBREVIATIONS

mL	milliliter
mm	millimeter
PID	photoionization detector
ppb	parts per billion
ppb v	parts per billion by volume
PVC	polyvinyl chloride
TCE	trichloroethylene
SVOC	semi-volatile organic compound
mg/L	microgram per liter
mL	microliter
VOC	volatile organic compound

Comparison of Vapor Concentrations of Volatile Organic Compounds with Ground-Water Concentrations of Selected Contaminants in Sediments Beneath the Sudbury River, Ashland, Massachusetts, 2000

By Jean P. Campbell, Forest P. Lyford, *and* Richard E. Willey

Abstract

A mixed plume of contaminants in ground water, including volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), and metals, near the former Nyanza property in Ashland, Massachusetts, discharges to the Sudbury River upstream and downstream of Mill Pond and a former mill raceway. Polyethylene-membrane vapor-diffusion (PVD) samplers were installed in river-bottom sediments to determine if PVD samplers provide an alternative to ground-water sampling from well points for identifying areas of detectable concentrations of contaminants in sediment pore water near the ground-water and surface-water interface. In August and September 2000, the PVD samplers were installed near well points at depths of 8 to 12 inches in both fine and coarse sediments, whereas the well points were installed at depths of 1 to 5 feet in coarse sediments only.

Comparison between vapor and water samples at 29 locations upstream from Mill Pond show that VOC vapor concentrations from PVD samplers in coarse river-bottom sediments are more likely to correspond to ground-water concentrations from well points than PVD samplers installed in fine sediments. Significant correlations based on Kendall's Tau were shown between vapor and ground-water concentrations for trichloroethylene and chlorobenzene for PVD samplers installed in coarse sediments where the fine organic layer that separated the two sampling depths was 1 foot or less in thickness.

VOC concentrations from vapor samples also were compared to VOC, SVOC, and metals concentrations from ground-water samples at 10 well points installed upstream and downstream from Mill Pond, and in the former mill raceway. Chlorobenzene vapor concentrations correlated significantly with ground-water concentrations for 5 VOCs, 2 SVOCs, and 10 metals. Trichloroethylene vapor concentrations did not correlate with any of the other ground-water constituents analyzed at the 10 well points. Chlorobenzene detected by use of PVD samplers appears to be a strong indicator of the presence of VOCs, SVOCs, and metals in ground water sampled from well points at this site.

Results from PVD samplers indicate that contaminant concentrations in water from well points installed 1 to 5 ft below fine sediments may not reflect concentrations in pore water less than 1 foot below the river bottom. There is insufficient information available to determine if VOC concentrations detected in PVD samplers are useful for identifying detectable aqueous concentrations of SVOCs and metals in sediment pore water at this site. Samples of pore water from a similar depth as PVD samplers are needed for confirmation of this objective.

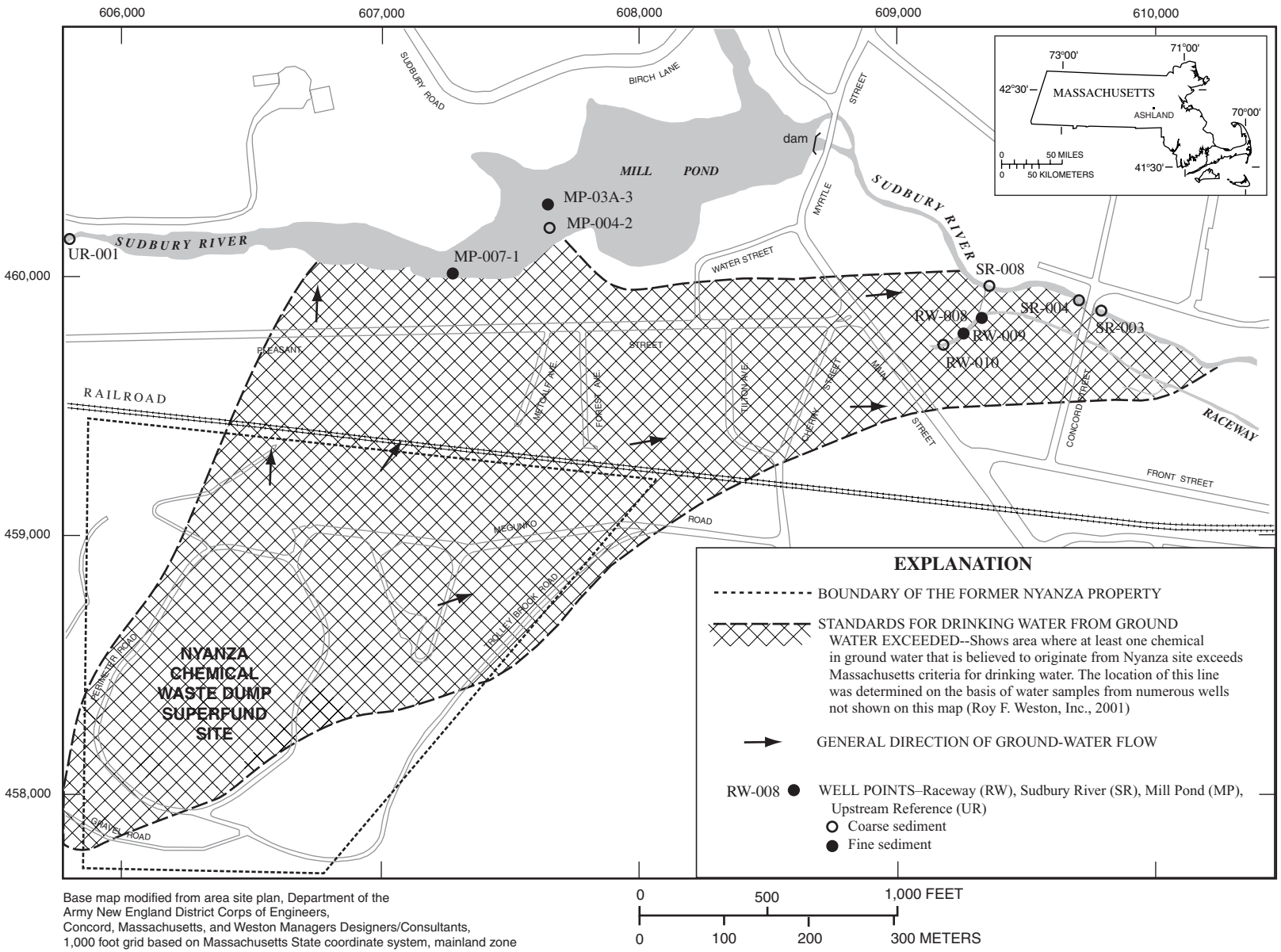
INTRODUCTION

Contaminant concentrations in sediment pore water beneath rivers differ by orders of magnitude because of variations in the character of the sediments, complex discharge patterns for ground water, and ongoing erosional and depositional processes. For these reasons, many pore-water samples from sediments are needed to evaluate contaminant threats to the environment. Methods that commonly are used to characterize sediment-pore-water contaminants include collection of samples from sediment, water from seepage meters, water from well points driven into bottom sediments, and use of diffusion samplers (D.B. Chadwick, Melanie Kito, and Amy Carlson, Space and Naval Warfare Systems Center, San Diego, Calif., written commun., 2001).

Where volatile organic compounds (VOCs) are present, the U.S. Geological Survey (USGS) has used polyethylene-membrane vapor-diffusion (PVD) samplers effectively in various New England settings to map the distribution of VOCs in sediment pore water (Lyford and others, 1999, 2000; Church and others, 2000; Savoie and others, 1999, 2000). PVD samplers have been used in previous studies primarily to determine the presence of VOCs where ground water discharges to surface water; however, VOC concentrations observed in vapor samples also have been useful for mapping relative concentrations of VOCs in pore water. Once VOC discharge areas are identified, these contaminated areas can be sampled by other methods to obtain quantitative contaminant concentrations. In areas where a mixture of chemicals, such as VOCs, semi-volatile organic compounds (SVOCs), and metals in ground water discharges to surface water and contaminates bottom sediments, PVD samplers may be an economical reconnaissance tool to identify areas contaminated by a variety of chemicals. Field tests are needed to determine if PVD samplers effectively can identify the presence (or approximate concentration) of other contaminants where mixed plumes of contaminants discharge to surface water.

A mixed plume of contaminants that includes VOCs, SVOCs, and metals in ground water near the former Nyanza, Inc., property in Ashland, Mass., discharges to the Sudbury River (Roy F. Weston, Inc., 1999) (fig. 1). A plan by Roy F. Weston, Inc. to sample ground water from well points beneath the Sudbury River in August and September 2000 as part of a toxicity-testing study provided an opportunity to compare analytical results from vapor samples to analytical results from ground-water samples at similar locations. A study was designed to collect vapor-sample data that would aid in identifying well-point locations and to collect data so that VOC concentrations detected in vapor samples could be compared to concentrations of VOCs, SVOCs, and metals detected in water samples from well points. This study was done to determine if PVD samplers could be used successfully as reconnaissance tools to identify areas contaminated by VOCs, SVOCs, and metals in river-bottom sediments, where a mixed plume of contaminants in ground water discharges to surface water.

This report presents the VOC data collected from PVD samplers installed in sediments beneath the Sudbury River in August and September 2000 and compares concentrations of VOCs detected in PVD samplers to concentrations of VOCs, SVOCs, and metals detected in water samples from well points. Also included in the report is an assessment of the two sampling methods used to characterize contaminants in river-bottom sediments in terms of effort, reliability of results, and hydrologic conditions at the site. For this report, the water sampled from PVD samplers at shallow depths, from 8 to 12 in., is called pore water; and the water sampled from well points at deeper depths, from 1 to 5 ft, is called ground water.



Base map modified from area site plan, Department of the Army New England District Corps of Engineers, Concord, Massachusetts, and Weston Managers Designers/Consultants, 1,000 foot grid based on Massachusetts State coordinate system, mainland zone

Figure 1. Location of 10 well points near Mill Pond, extent of contaminants in ground water, and direction of ground-water flow, Ashland, Massachusetts.

DESCRIPTION OF STUDY AREA

The study area includes reaches of the Sudbury River upstream and downstream from Mill Pond and a former mill raceway downstream from Mill Pond in Ashland, Mass. These study reaches are discussed here as being near Mill Pond. Reaches of the Sudbury River included in the study extend from the entrance to Mill Pond upstream about 2,000 ft and from Mill Pond dam downstream to the east side of the Concord Street bridge (fig. 1). The upstream end of Mill Pond, near sampler location 1A is called the entrance to Mill Pond in this report (figs. 2 and 3). The study reach of the raceway extends from its origin near Main Street for about 200 ft downstream. The Sudbury River at a former USGS streamflow gaging station about 0.8 mi downstream from the Mill Pond dam has a drainage area of 35.1 mi^2.

The ground-water system in this area includes glacial lake deposits, till, and fractured granite. Materials in the glacial lake deposits range in size from silt to sand and gravel. The depth to bedrock increases eastward from less than 30 ft upstream from Mill Pond to nearly 80 ft in an east-west trending trough downstream from the dam (Ebasco Services, Inc., 1991).

The Sudbury River sediments observed during this study range in size from fine-grained materials such as organic matter and silt, to coarse gravel and cobbles. In most transects, the center of the stream channel, an area along the southern bank from about 200 to 400 ft upstream from the pond, and an area along the northern bank from about 600 to 800 ft upstream from the pond, the sediments are predominantly gravel. Gravel and cobbles were observed from about 1,200 to 1,500 ft upstream from the pond and in the upstream reference area (UR-001, fig. 1). The sediments downstream from the Mill Pond dam also are composed of coarse bottom materials. The sediments in the former mill raceway are fine organic materials over cobbles.

The former Nyanza property is the principal source of ground-water contamination in the study area (Roy F. Weston, Inc., 1998). Ground water from the

Nyanza property flows northward toward Mill Pond and eastward toward the Sudbury River downstream from Mill Pond and the former mill raceway. A contaminant plume attributed to waste-disposal activities at the former Nyanza property discharges to the Sudbury River throughout much of the study area (fig. 1). Mill Pond is a recharge source to ground water along its southern and eastern sides. This recharge to ground water limits the northern extent of the plume.

Contaminants in ground water near the Nyanza property include VOCs, SVOCs, and metals. Specific contaminants that have been detected in water from wells installed in glacial sediments and bedrock include the organic chemicals aniline, benzidine, nitrobenzene, chlorobenzene, dichlorobenzene, trichlorobenzene, and trichloroethylene (TCE), and the inorganic chemicals arsenic, beryllium, chromium, cobalt, manganese, mercury, and sodium (Roy F. Weston, 2001, p. 2–5). Water sampling from seepage meters installed in sediments along the Sudbury River, Mill Pond, and raceway detected all of these contaminants except chromium (Roy F. Weston, Inc., 1999). TCE and chlorobenzene are the principal VOCs detected in ground water at this study site. Previous tests of PVD samplers in the study area detected maximum vapor concentrations of 1,910 ppb v for TCE, 5,330 ppb v for chlorobenzene, and 54 ppb v for benzene. The concentrations of these VOCs in vapor correlated well with concentrations in water samples collected from seepage meters about 5 to 6 ft away. The highest concentrations detected for these three VOCs were in the reach of the Sudbury River upstream from Mill Pond (Lyford and others, 2000).

Streamflow during the study period at the USGS streamflow gaging station, Sudbury River at Saxonville, Mass., about 9 mi downstream from Mill Pond, was normal or slightly above normal from August 15 to 20, 2000, and below normal from August 21 to September 12. Rainfall on August 16, August 23, and September 2 ranged from 0.24 to 0.30 in., measured at the National Weather Service climatological station in Worcester, Mass., about 20 mi west of the study area. This rainfall caused slight increases in daily streamflow (fig. 4).

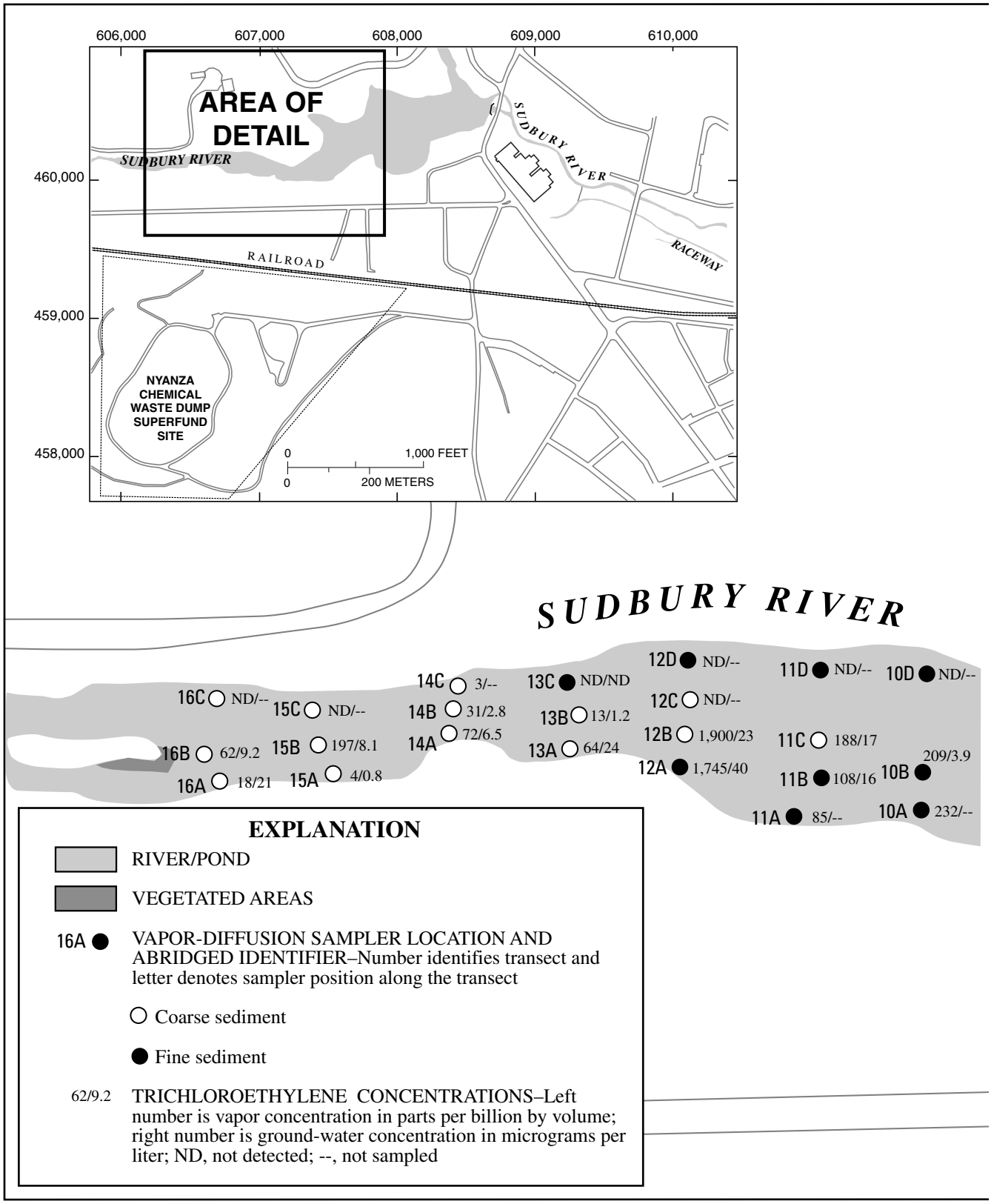


Figure 2. Vapor-diffusion sampler locations and trichloroethylene concentrations from vapor and ground-water samples upstream from Mill Pond, Ashland, Massachusetts. Data for water samples from Roy F. Weston, Inc., 2001.

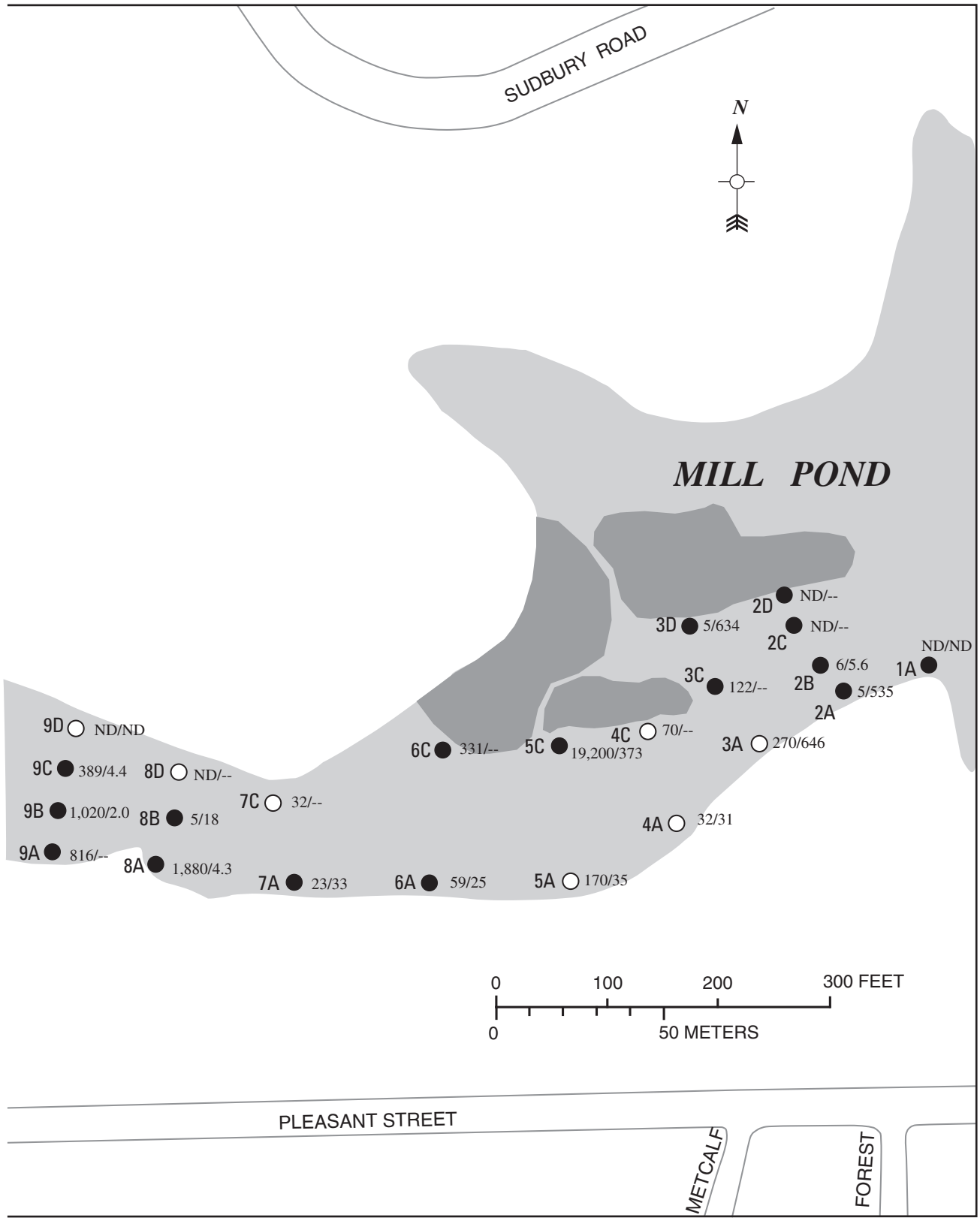


Figure 2. Vapor-diffusion sampler locations and trichloroethylene concentrations from vapor and ground-water samples upstream from Mill Pond, Ashland, Massachusetts. Data for water samples from Roy F. Weston, Inc., 2001—*Continued.*

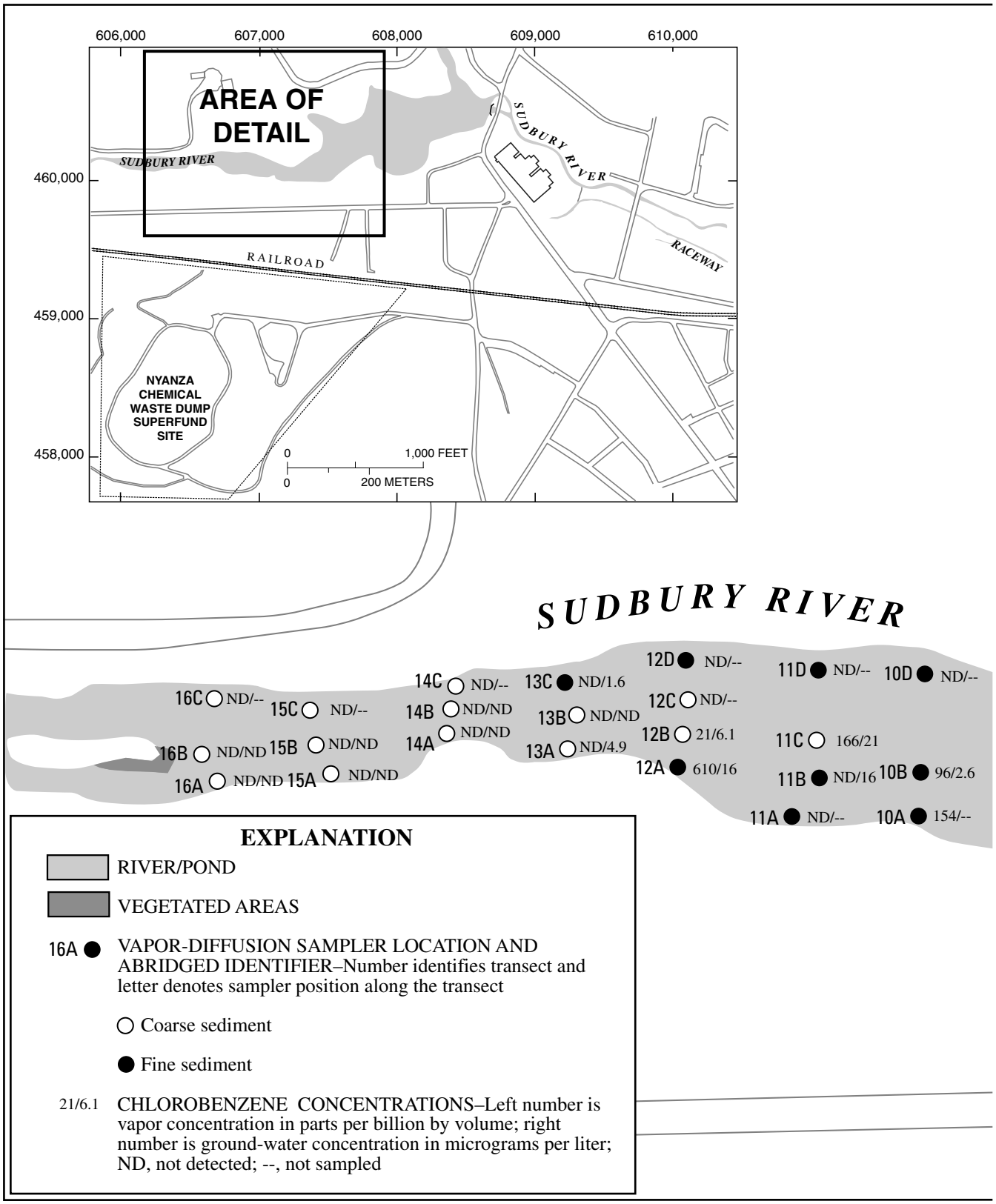


Figure 3. Vapor-diffusion sampler locations and chlorobenzene concentrations from vapor and ground-water samples upstream from Mill Pond, Ashland, Massachusetts. Data for water samples from Roy F. Weston, Inc., 2001.

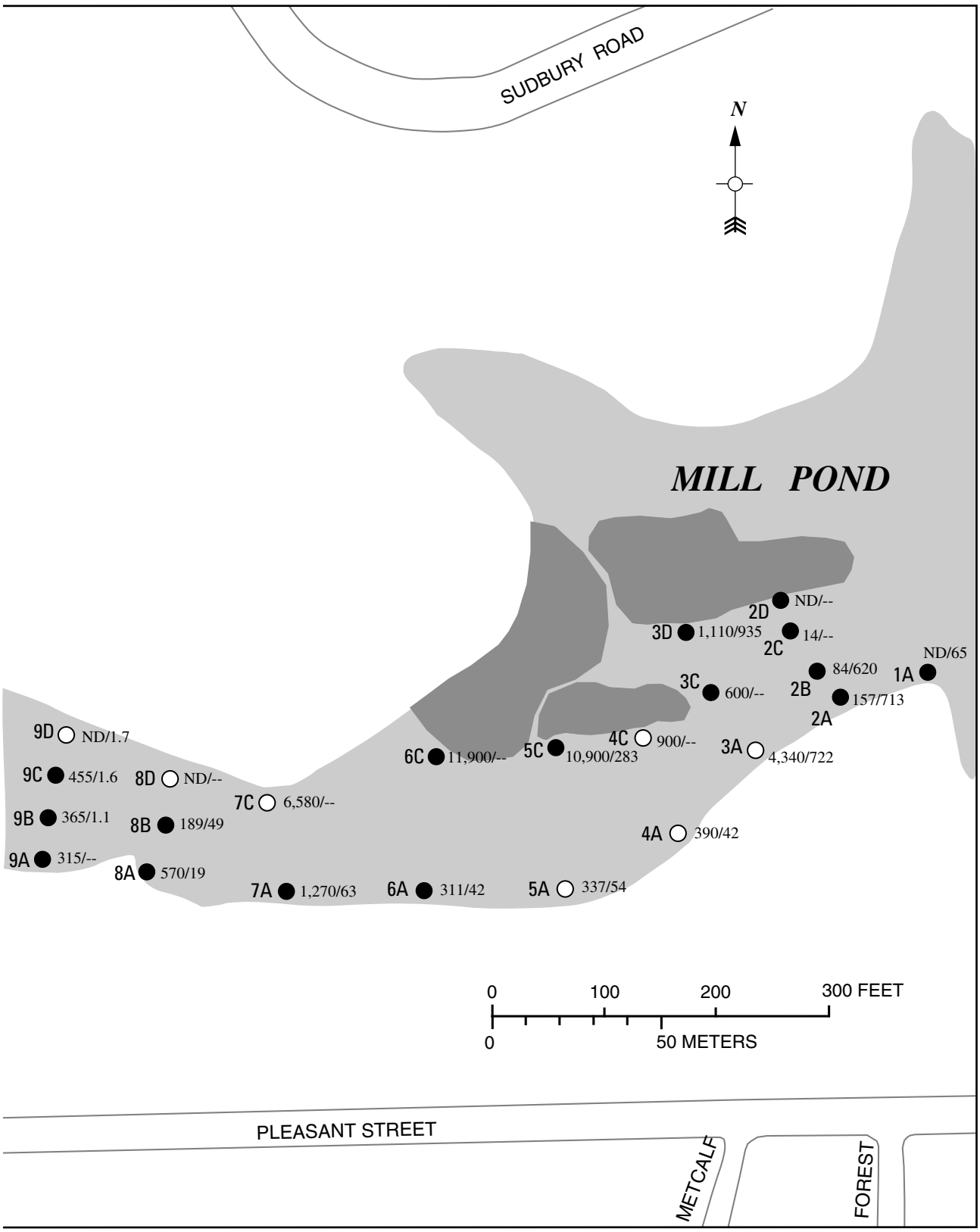


Figure 3. Vapor-diffusion sampler locations and chlorobenzene concentrations from vapor and ground-water samples upstream from Mill Pond, Ashland, Massachusetts. Data for water samples from Roy F. Weston, Inc., 2001—*Continued*.

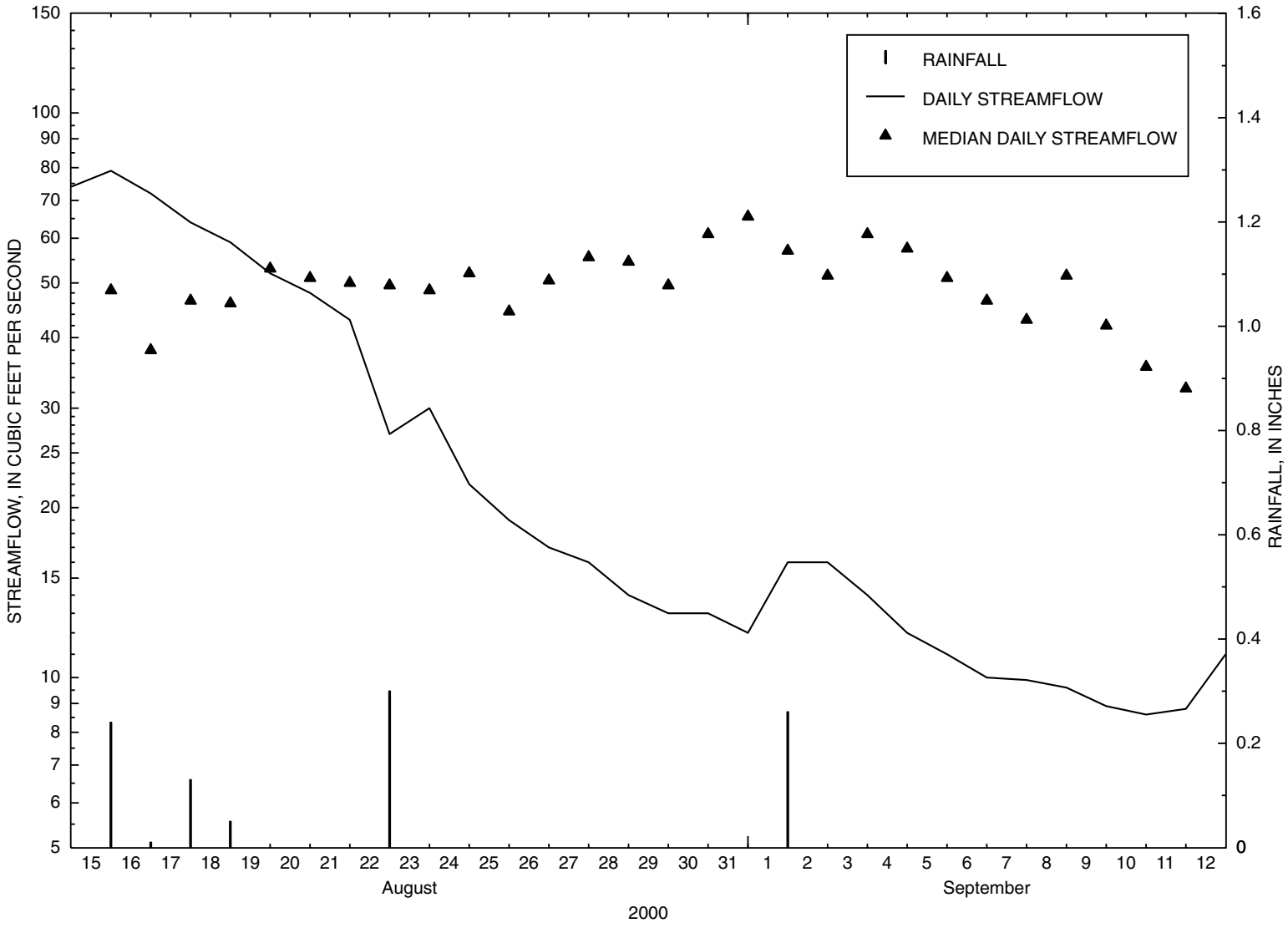


Figure 4. Daily and median daily streamflow for the Sudbury River at Saxonville, Massachusetts, and rainfall at Worcester, Massachusetts, August and September 2000. Median daily streamflow is based on 19 years of record.

STUDY DESIGN

This study was designed to coincide with a study designed and implemented by Roy F. Weston, Inc., (Weston) under a contract with the U.S. Army Corps of Engineers. The purpose of the Weston study, which was designed in two phases, was to test ground-water toxicity on aquatic organisms. For the first phase, ground-water samples were collected from a network of temporary well points and analyzed for VOCs to identify contaminant zones. For the second phase, nine well points were installed (or selected from the existing temporary well points) upstream and downstream of Mill Pond and in the former mill raceway in selected contaminated locations identified during the phase one investigation, and in one uncontaminated location. Sampling and installation dates for the first and second study phases are summarized in table 1.

The USGS installed PVD samplers upstream from Mill Pond on August 15–17, 2000, about 2 weeks before the installation of well points to allow time for the samplers to equilibrate with VOCs in the sediment pore water (figs. 2 and 3). Retrieval of the PVD samplers was to coincide approximately with the collection of water samples. The USGS installed 50 samplers at two to four locations along 16 transects across the river, upstream from Mill Pond. Locations of PVD samplers included the northern bank of the river where contamination was considered unlikely and ground-water sampling was not initially planned due to financial and time constraints. At five locations, PVD samplers were lost prior to or during recovery. Locations of samplers recovered are shown in figures 2 and 3.

Most vapor samples were analyzed at an on-site laboratory prior to collection of ground-water samples to help prioritize the installation of well points and increase the possibility that locations of highest contaminant concentrations were sampled. Upon retrieval of PVD samplers, either a wire survey flag or fishing bobber attached to a plastic bag filled with sand marked the sampling locations. A total of 29 ground-water samples were collected upstream from Mill Pond near locations of PVD samplers. Water samples collected within about 5 ft of PVD samplers are considered to be collocated. Weston personnel also collected water samples from temporary well points installed beneath the Sudbury River and former mill raceway downstream from Mill Pond dam for the first study phase.

Well-point sampling results from the first study phase were used to select locations of nine well points for further study that represented the range of contaminant concentrations detected in three settings near Mill Pond: the Sudbury River upstream from Mill Pond, the raceway, and the Sudbury River downstream from the dam. A tenth well point was installed upstream of the known extent of the contaminant plume to provide samples of uncontaminated water. PVD samplers were installed within 1 ft of the well points. Water samples collected from the well points were analyzed for VOCs, SVOCs, and metals and used for laboratory toxicity tests. Plans originally called for three sets of water samples from the well points throughout a 1-week period to replenish water for toxicity tests. Because of a high mortality rate for organisms in water obtained from 7 wells, only 3 out of 10 wells were sampled three times (Roy F. Weston, Inc, 2000). PVD samplers were removed simultaneously with Weston's last sampling round after they had been in place for 6 days.

Table 1. Sampling and installation dates for polyethylene-membrane vapor-diffusion samplers and well points upstream from Mill Pond (first study phase) and at four areas near Mill Pond (second study phase), Ashland, Massachusetts, August-September 2000

[Well point samples collected by R.F. Weston, Inc.; PVD, polyethylene-membrane vapor-diffusion; I, PVD sampler installed; V, vapor sample collected; W, water sample collected; shaded area denotes equilibration period; water samples on September 10 and 12 are repeated samplings for selected well points]

Sampling phase and sample type	August 2000																		September 2000												
	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	1	2	3	4	5	6	7	8	9	10	11	12	13
First Study Phase																															
PVD samplers		I	I	I											V	V															
Well points																W	W	W	W												
Second Study Phase																															
PVD samplers																								I						V	
Well points																									W			W		W	

STUDY METHODS

Study methods described in this section include construction, installation, and retrieval of PVD samplers, analysis of vapor in samples from PVD samplers, collection of water samples by Weston personnel, analysis of water samples, quality assurance, and statistical analysis of the water-quality data.

Polyethylene-Membrane Vapor-Diffusion Samplers

PVD samplers allow VOCs in water to diffuse through a semipermeable polyethylene membrane until the contaminant concentrations in the air inside the sampler reach equilibrium with the contaminant concentrations in the sediment pore water (Savoie and others, 1999). The time required for the PVD samplers to equilibrate, which varies with the rate of water movement through the sediments, depends on the time required for the river-bottom sediments to return to ambient conditions after the disturbance caused by installation of the samplers. Concentrations of VOCs in samplers can stabilize within 12 to 24 hours in highly permeable sediments but may require more than 65 hours in sediments with low permeability. Equilibration also takes longer as ground-water temperature decreases (D.A. Vroblesky, U.S. Geological Survey, written commun., 2000, 2001). An equilibration period of about 2 weeks generally is considered adequate for most investigations.

Construction of Samplers

PVD samplers were constructed on the basis of methods modified slightly from those described by Savoie and others (1999). A PVD sampler consists of an uncapped 40-mL glass vial inside a 4-mil thick polyethylene sleeve, heat sealed at one end. After the air is removed from the sleeve, the other end is sealed. The excess length of sleeve is folded over the vial to form a tight single-layer seal before the vial is placed into a second sleeve. The second sleeve protects the vial from water and sediment and also is sealed at both ends. The sampler is fastened (open end down) with cable ties to a wire survey flag. Duplicate samplers are constructed in the same manner, except that two samplers are attached onto one survey flag.

Installation and Retrieval of Samplers

One of two methods was used to install samplers, depending on river depth. Samplers were installed at a depth of 8 to 12 in. beneath the river bottom by either method. In water depths less than 2 ft, samplers were installed manually into a hole made by wedging a narrow-bladed shovel into the sediments. In water depths greater than 2 ft, a drive-pipe assembly, which consisted of a 2-in. outer pipe and a 1.5-in. inner pipe with a pointed tip, was used to install the samplers. The entire assembly is driven into the bottom sediments with a sledge or slide hammer. At about 1 ft below the river bottom, the inner pipe is removed and the sampler is pushed to the bottom of the outer pipe by a 1-in. polyvinyl chloride (PVC) pipe. When the outer pipe is removed, the sediments collapse around the sampler. Many samplers were installed with the drive-pipe assembly from a rowboat because water depths exceeded 3 ft. Where water was 2.5 ft or deeper, samplers were marked by attaching a fish bobber to the wire survey flag.

Upon retrieval of a sampler, the outer polyethylene sleeve is removed and a septum cap is placed immediately on the bottle over the inner sleeve. The sample is labeled and then chilled to 4˚C until analyzed at a field or fixed laboratory. PVD samplers installed upstream from Mill Pond for the first study phase were retrieved on August 28 and 29 after an equilibration period of 11 to 14 days. Samplers installed near the 10 well points for the second study phase were retrieved September 12 after an equilibration period of 6 days.

Analysis of Vapor Samples

Vapor samples collected with PVD samplers upstream from Mill Pond were analyzed in a mobile laboratory on site within 10 hours of retrieval with the USEPA Region I standard air-screening method (U.S. Environmental Protection Agency, 2000). A Photovac 10A10 field portable gas chromatograph (GC) equipped with a 4-ft by 1/8-in. SE-30 column and a photoionization detector (PID), and a Shimadzu GC 14A equipped with a 30 m, 0.53 mm DBPS-624 column, and a PID and electron capture detector were used to analyze vapor samples.

Air-standard concentrations were developed by the USEPA Region I laboratory to calibrate GCs for specific vapor constituents. Vapor concentrations in the headspace above a 10 ppb aqueous solution at about

1˚C were used as calibration standards. Standards, prepared at a 10 ppb concentration, were kept chilled prior to calibration for vapor-sample analyses. Vapor samples were stored on ice immediately after collection and were kept at a similar temperature to the calibration standard when analyzed. Samples were analyzed by injecting a needle through the cap septum and polyethylene sleeve to withdraw 200 µL of vapor to be injected into the GC port. Target compounds for the vapor-sample analyses by the mobile laboratory and reporting limits (in parentheses) were TCE (5 ppb v), chlorobenzene (20 ppb v), benzene (10 ppb v), toluene (30 ppb v), tetrachloroethylene (2 ppb v), and 1,1,1-trichloroethane (5 ppb v).

Vapor samples collected near the 10 well points sampled for the second study phase were retrieved, capped, labeled, and chilled in the same manner as the samples collected for the first study phase. These samples were transported on ice to the USEPA Region I laboratory and were analyzed with the standard air-screening method with a Photovac GC (U.S. Environmental Protection Agency, 2000). Target compounds for the vapor-sample analyses and reporting limits (in parentheses) were TCE (14 ppb v), chlorobenzene (100 ppb v), and benzene (15 ppb v).

Quality Assurance and Quality Control

Field duplicates were prepared to evaluate data precision, and trip blanks were used to evaluate potential contamination. Duplicate PVD samplers were installed at eight locations listed in table 2. Field duplicates are paired PVD samplers with a 1-in. lateral distance between the openings of the glass vials; therefore, variability between the two samples is not because of site location. Trip blanks identify potential contamination caused by sample handling, storage, and (or) laboratory analysis. Two trip blanks were submitted with samples for on-site analysis for the first study phase, and one trip blank was submitted with samples analyzed by the USEPA Region I laboratory for the second study phase.

Table 2. Concentration and relative percent difference between field duplicate sample pairs for chlorobenzene and trichloroethylene from vapor samples near Mill Pond, Ashland, Massachusetts

[**Relative percent difference:** The relative percent difference should be less than 30 percent, according to the U.S. Environmental Protection Agency's measurement performance criteria for duplicate samples. Concentrations are in parts per billion by volume. No., number; <, less than]

Sample No.	Date of retrieval	Time of retrieval	Chlorobenzene			Trichloroethylene		
			Concentration		Relative percent difference	Concentration		Relative percent difference
			Sample 1	Sample 2		Sample 1	Sample 2	
MP-002-D	8-28-00	1044	<20	<20	0	<5	<5	0
MP-005-A	8-28-00	1144	156	337	73	157	170	8
MP-008-A	8-28-00	1154	570	550	4	1,880	1,440	26
MP-008-D	8-28-00	1521	<20	<20	0	<5	<5	0
MP-010-D	8-28-00	1502	<20	<20	0	<5	<5	0
MP-011-B	8-28-00	1319	<20	<20	0	108	108	0
MP-013-C	8-28-00	1422	<20	<20	0	<5	<5	0
SR-004	9-12-00	0850	7,800	5,500	35	11,000	10,000	10

Quality-assurance protocols for the field and fixed laboratories are described in the USEPA Region I standard air-screening method (U.S. Environmental Protection Agency, 2000). To comply with these protocols laboratory duplicates, standards and second-source quality-control standards, and laboratory blanks were prepared and analyzed by both laboratories.

Collection and Analysis of Ground-Water Samples

Weston personnel installed about 40 PVC temporary well points in the area upstream from Mill Pond with a barge-mounted Geoprobe rig (Roy F. Weston, Inc., 2001). A 4-ft sediment core sample was collected to determine the depth interval for the well-point screen. Well-point screens, 2-ft long, were installed in coarse granular deposits and centered from 2 to 4 ft beneath the river bottom depending on the thickness of the fine organic layer, which ranged from none present to 3 ft. Organic layers typically are thickest along stream banks and downstream of islands or vegetated areas where stream velocities are low. Water samples from the temporary well points represent water-quality conditions about 1 to 5 ft below the bottom of the Sudbury River. The well points were purged with a peristaltic pump for about 15 minutes prior to sample collection.

Weston personnel replaced three temporary PVC well points with steel well points in the area upstream from Mill Pond for the second study phase. The well-point screens were 2-ft long and centered about 1.5 ft below the fine organic layer, if present. The well points used for the second study phase in the areas downstream from the Mill Pond dam and the former mill raceway were selected from the temporary well points installed during the first study phase. Well points in the upstream reference area, the Sudbury River downstream from the dam, and in the raceway were installed by manually driving a well point into the stream bottom. Water samples from these well points also represent water-quality conditions from about 1 to 5 ft below the river bottom.

Water samples from temporary well points were collected and processed in accordance with the sampling protocol for headspace samples (U.S. Environmental Protection Agency, 1998). The samples were analyzed within 24 hours for TCE, chlorobenzene, and *cis*-1,2-dichloroethylene. VOC concentrations in the headspace samples were analyzed with the same portable GCs used to analyze vapor samples. For headspace samples, a GC is calibrated with an aqueous standard of known concentration; thus, headspace-vapor concentrations are reported in micrograms per liter. The calibration standard and the water in the headspace sample are brought to the ambient air temperature in the laboratory. The analyst pours off about 10 ml of water from a vial, recaps it, and allows time for the sample to equilibrate. VOCs present in the water sample are driven out of solution into the vapor phase by keeping the sample at ambient temperature.

The number of times the 10 well points for the second study phase were sampled, from 1 to 3, depended on the toxicity-testing results. These ground-water samples were analyzed for VOCs, SVOCs, and metals by a commercial laboratory.

Statistical Methods

The correlation between vapor and ground-water concentrations was assessed with Kendall's Tau (Helsel and Hirsch, 1992). Kendall's Tau was used because it is a nonparametric test that does not require a normal distribution of the data, and it is good for small sample sizes. Tau computes the significance level of the correlation on the basis of ranks of the data and not the specific values; therefore, it is an appropriate statistical test for data sets that include concentrations less than the reporting limit. A significance level (p-value) of less than 0.1000 was considered a significant correlation between groups of data for this report.

QUALITY-ASSURANCE RESULTS FOR VAPOR SAMPLES

Concentrations of duplicate sample pairs and the relative percent difference are shown in table 2. The relative percent difference between sample pairs should be less than 30 percent, according to USEPA's measurement-performance criteria for field duplicates. The eight differences calculated for TCE were less than 30 percent, but two out of eight samples for chlorobenzene showed differences greater than 30 percent. In general, concentrations in field duplicates were the same order of magnitude between sample pairs, which demonstrates the repeatability of VOC concentrations in vapor samples. Factors that cause differences between duplicates may include slightly different exposure times (1 or 2 minutes) to air after retrieval and before capping and subtle variations in construction that might affect equilibration time. These factors may cause measured concentrations to be lower than actual concentrations. For this reason, the highest concentration of VOCs observed in duplicate samples are considered to be most representative of VOCs in pore water, and were used for interpretations and statistical analysis.

Target compounds were not detected in the two trip blanks submitted to the USEPA mobile laboratory, which indicates no contamination was introduced into these samples in the field or the laboratory. Target compounds also were not detected in the trip blank submitted to the USEPA Region I laboratory.

COMPOUNDS DETECTED IN VAPOR SAMPLES UPSTREAM FROM MILL POND

VOCs were detected in many of the PVD samplers installed upstream from Mill Pond during the first study phase. Analytical results from PVD samplers are called vapor concentrations and results observed in water from well points are called ground-water concentrations. TCE was detected from the southern bank of the Sudbury River to the center of the channel from transects 8 to 16 and along both banks in transects 3 to 7 (table 3, fig. 2). The northern end of transects 1 to 6 is the southern edge of wetland vegetation dominated by purple loosestrife (*Lythrum salicaria*). Elsewhere, the northern end is the northern bank of the river channel. The TCE plume extends at least 300 ft further upstream from the area of ground-water contamination shown in figure 1. The upstream extent of the TCE plume is not known, but may be between sampler location UR-001 (fig. 1) and transect 16 (figs. 2 and 3). TCE concentrations greater than 180 ppb v were detected in vapor samples in a 400-ft wide area from transects 8 to 12. Concentrations greater than 180 ppb v also were detected in individual samples collected in transects 3, 5, 6, and 15 (fig. 2).

Chlorobenzene was detected from the southern bank to the center of the channel from transects 8 to 12 and along both banks from transects 3 to 7 (table 3, fig. 3). Chlorobenzene was not detected along the northern bank from transects 8 to 16. The upstream extent of detectable concentrations of chlorobenzene is between transects 12 and 13. Chlorobenzene concentrations greater than 300 ppb v were detected in vapor samples in a 600-ft wide area from transects 3 to 9, and in the sample collected at 12A.

Table 3. Concentration of selected volatile organic compounds from vapor and ground-water samples at the Sudbury River upstream from Mill Pond, Ashland, Massachusetts

[Data for water samples and depth of organic layer from Roy F. Weston, Inc. (2001). Brackets denote collocated samples. **Sample type:** V, vapor-sample concentrations in parts per billion by volume; W, water-sample concentrations in micrograms per liter. **Volatile organic compound:** Compound not detected at the reporting limit in parentheses. L, observed concentration is below the reporting limit. d, duplicate of preceding sample; --, not analyzed]

Sample location (figs. 2 and 3)	Date of collec-tion	Sediment type	Organic layer thickness in feet	Sample type	Volatile organic compound				
					Benzene	Chloro-benzene	Tetrachloro-ethylene	Toluene	Trichloro-ethylene
MP-001-A	8-28-00	Fine	--	V	(10)	(20)	(2)	(30)	(5)
MP-001-1	8-29-00	Coarse	2	W	--	65	--	--	(0.5)
MP-002-A	8-28-00	Fine	--	V	(10)	157	(2)	(30)	5
MP-002-1	8-30-00	Coarse	1	W	--	713	--	--	535
MP-002-B	8-28-00	Fine	--	V	(10)	84	(2)	(30)	6
MP-002-2	8-29-00	Coarse	1	W	--	620	--	--	5.6
MP-002-C	8-28-00	Fine	--	V	(10)	14L	(2)	(30)	(5)
MP-002-D	8-28-00	Fine	--	V	(10)	(20)	(2)	(30)	(5)
MP-002-D-d	8-28-00	Fine	--	V	(10)	(20)	(2)	(30)	(5)
MP-003-A	8-28-00	Coarse	--	V	248	4,340	(2)	43	270
MP-003-1	8-30-00	Coarse	0	W	--	722	--	--	646
MP-003-C	8-28-00	Fine	--	V	65	600	(2)	(30)	122
MP-003-D	8-28-00	Fine	--	V	151	1,110	(2)	30	5
MP-003-3	9-01-00	Coarse	2	W	--	935	--	--	634
MP-004-A	9-12-00	Coarse	--	V	8L	390	(2)	(30)	32
MP-004-1	8-30-00	Coarse	0.5	W	--	42	--	--	31
MP-004-C	8-29-00	Coarse	--	V	(10)	900	(2)	(30)	70
MP-005-A	8-28-00	Coarse	--	V	(10)	156	(2)	(30)	157
MP-005-A-d	8-28-00	Coarse	--	V	(10)	337	(2)	(30)	170
MP-005-1	8-30-00	Coarse	0.5	W	--	54	--	--	35
MP-005-C	8-29-00	Fine	--	V	(10)	10,900	3	(30)	19,200
MP-005-3	9-01-00	Coarse	1	W	--	283	--	--	373
MP-006-A	8-28-00	Fine	--	V	(10)	311	(2)	(30)	59
MP-006-1	8-30-00	Coarse	1	W	--	42	--	--	25
MP-006-C	8-29-00	Fine	--	V	(10)	11,900	(2)	40	331
MP-007-A	8-28-00	Fine	--	V	(10)	1,270	(2)	194	23
MP-007-1	8-30-00	Coarse	1	W	--	63	--	--	33
MP-007-C	8-29-00	Coarse	--	V	(10)	6,580	(2)	40	32
MP-008-A	8-28-00	Fine	--	V	(10)	570	(2)	(30)	1,880
MP-008-A-d	8-28-00	Fine	--	V	(10)	550	(2)	(30)	1,440
MP-008-1	8-31-00	Coarse	2	W	--	19	--	--	4.3
MP-008-B	8-28-00	Fine	--	V	(10)	189	(2)	(30)	5
MP-008-2	8-31-00	Coarse	3	W	--	49	--	--	18
MP-008-D	8-28-00	Coarse	--	V	(10)	(20)	(2)	(30)	(5)
MP-008-D-d	8-28-00	Coarse	--	V	(10)	(20)	(2)	(30)	(5)
MP-009-A	8-28-00	Fine	--	V	(10)	315	(2)	(30)	816

Table 3. Concentration of selected volatile organic compounds from vapor and ground-water samples at the Sudbury River upstream from Mill Pond, Ashland, Massachusetts—*Continued*

Sample location (figs. 2 and 3)	Date of collec-tion	Sediment type	Organic layer thickness in feet	Sample type	Volatile organic compound				
					Benzene	Chloro-benzene	Tetrachloro-ethylene	Toluene	Trichloro-ethylene
MP-009-B	8-28-00	Fine	--	V	(10)	365	(2)	(30)	1,020
MP-009-1	8-31-00	Coarse	2.5	W	--	1.1	--	--	2.0
MP-009-C	8-28-00	Fine	--	V	(10)	455	(2)	(30)	389
MP-009-2	8-31-00	Coarse	3	W	--	1.6	--	--	4.4
MP-009-D	8-28-00	Coarse	--	V	(10)	(20)	(2)	(30)	(5)
MP-009-3	9-01-00	Coarse	0.5	W	--	1.7	--	--	(0.5)
MP-010-A	8-28-00	Fine	--	V	(10)	154	(2)	(30)	232
MP-010-B	8-28-00	Fine	--	V	(10)	96	(2)	(30)	209
MP-010-1	8-31-00	Coarse	3	W	--	2.6	--	--	3.9
MP-010-D	8-28-00	Fine	--	V	(10)	(20)	(2)	(30)	(5)
MP-010-D-d	8-28-00	Fine	--	V	(10)	(20)	(2)	(30)	(5)
MP-011-A	8-28-00	Fine	--	V	(10)	(20)	(2)	(30)	85
MP-011-B	8-28-00	Fine	--	V	(10)	(20)	(2)	(30)	108
MP-011-B-d	8-28-00	Fine	--	V	(10)	(20)	(2)	(30)	108
MP-011-1	8-31-00	Coarse	1	W	--	16	--	--	16
MP-011-C	8-28-00	Coarse	--	V	16	166	(2)	(30)	188
MP-011-2	8-31-00	Coarse	0.5	W	--	21	--	--	17
MP-011-D	8-28-00	Fine	--	V	(10)	(20)	(2)	18L	(5)
MP-012-A	8-28-00	Fine	--	V	58	610	(2)	(30)	1,745
MP-012-1	8-31-00	Coarse	1	W	--	16	--	--	40
MP-012-B	8-28-00	Coarse	--	V	(10)	21	(2)	(30)	1,900
MP-012-2	8-31-00	Coarse	0	W	--	6.1	--	--	23
MP-012-C	8-28-00	Coarse	--	V	(10)	(20)	(2)	(30)	(5)
MP-012-D	8-28-00	Fine	--	V	(10)	(20)	(2)	(30)	(5)
MP-013-A	8-28-00	Coarse	--	V	(10)	(20)	(2)	(30)	64
MP-013-1	8-31-00	Coarse	2	W	--	4.9	--	--	24
MP-013-B	8-28-00	Coarse	--	V	(10)	(20)	(2)	(30)	13
MP-013-2	8-31-00	Coarse	0	W	--	(1.0)	--	--	1.2
MP-013-C	8-28-00	Fine	--	V	(10)	(20)	(2)	167	(5)
MP-013-C-d	8-28-00	Fine	--	V	(10)	(20)	(2)	588	(5)
MP-013-3	9-01-00	Coarse	1	W	--	1.6	--	--	(0.5)
MP-014-A	8-28-00	Coarse	--	V	(10)	(20)	(2)	(30)	72
MP-014-1	9-01-00	Coarse	0	W	--	(1.0)	--	--	6.5
MP-014-B	8-28-00	Coarse	--	V	(10)	(20)	(2)	(30)	31
MP-014-2	8-31-00	Coarse	0	W	--	(1.0)	--	--	2.8
MP-014-C	8-28-00	Coarse	--	V	(10)	(20)	(2)	(30)	3L
MP-015-A	8-28-00	Coarse	--	V	16	(20)	(2)	(30)	4L
MP-015-1	8-31-00	Coarse	0	W	--	(1.0)	--	--	0.8
MP-015-B	8-28-00	Coarse	--	V	(10)	(20)	1.4L	(30)	197
MP-015-2	8-31-00	Coarse	0	W	--	(1.0)	--	--	8.1
MP-015-C	8-28-00	Coarse	--	V	(10)	(20)	(2)	53	(5)

Table 3. Concentration of selected volatile organic compounds from vapor and ground-water samples at the Sudbury River upstream from Mill Pond, Ashland, Massachusetts—*Continued*

Sample location (figs. 2 and 3)	Date of collection	Sediment type	Organic layer thickness in feet	Sample type	Volatile organic compound				
					Benzene	Chlorobenzene	Tetrachloroethylene	Toluene	Trichloroethylene
MP-016-A	8-28-00	Coarse	--	V	(10)	(20)	(2)	(30)	18
MP-016-1	8-31-00	Coarse	0	W	--	(1.0)	--	--	21
MP-016-B	8-28-00	Coarse	--	V	(10)	(20)	(2)	(30)	62
MP-016-2	8-31-00	Coarse	1	W	--	(1.0)	--	--	9.2
MP-016-C	8-28-00	Coarse	--	V	(10)	(20)	(2)	(30)	(5)

COMPARISON OF VOLATILE ORGANIC COMPOUNDS IN VAPOR AND GROUND-WATER SAMPLES

Chlorobenzene and trichloroethylene concentrations were selected for comparison of results from collocated PVD samplers and temporary well points. Three other target VOCs (benzene, toluene, and tetrachloroethylene) were detected in a few samples but not enough for statistical comparisons.

A comparison of VOCs detected by the two methods indicates that TCE was present in 26 of 29 samples, and absent in the remaining three samples for both sample types (table 3). In these same 29 samples, chlorobenzene was present in 17 and absent in 7; 5 samples had ground-water concentrations that ranged from 1.6 to 65 µg/L, but had no detectable vapor concentration.

High vapor concentrations for the 29 collocated samples do not correspond to high ground-water concentrations for TCE and chlorobenzene (table 3, figs. 2 and 3). Chlorobenzene vapor concentrations in coarse sediments are more likely to correspond to ground-water concentrations than vapor concentrations in fine sediments (fig. 5*A*). Chlorobenzene concentrations greater than 100 µg/L in ground water were detected in transects 2, 3, and 5 (fig. 3). The areal extent of chlorobenzene is similar for ground water and vapor in these transects.

The lack of correlation between TCE concentrations in vapor and ground water for all collocated samples is shown in figure 5*B*. TCE vapor concentrations are lower than or similar to ground-water concentrations at five sample locations in transects 2 through 4 (fig. 2). Ground-water TCE concentrations are greater than 100 µg/L from transects 2 to 5, where vapor TCE data indicate only isolated elevated concentrations (greater than 150 ppb v), and minor concentrations (less than 10 ppb v) in transect 2. Ground-water data indicate low concentrations (40 µg/L or less) from transects 8 to 12, the area of four high (greater than 1,000 ppb v) vapor concentrations. Ground-water TCE contamination also was detected along the southern bank and in the center of the channel from transects 13 to 16, similar to the distribution observed in vapor.

Relations between vapor and ground-water concentrations generally were not significant when all samples were considered; however, significant relations were found when samples were segregated by sediment type or when only chlorobenzene was considered. Significant relations by Kendall's Tau statistical test were found between vapor and ground-water concentrations for TCE and chlorobenzene where PVD samplers and well points were both installed in coarse sediments (table 4, figs. 5*A* and *B*). The relation among all collocated chlorobenzene samples upstream from Mill Pond is good (p-value = 0.0003), partly because of the large number of samples with values less than the reporting limit for both vapor and ground-water samples. Significant relations also were observed where vapor samplers were installed in coarse or fine sediments when a fine organic layer 1 ft or less separated the sample depths (TCE p-value = 0.0071, chlorobenzene p-value = 0.0001, n = 21).

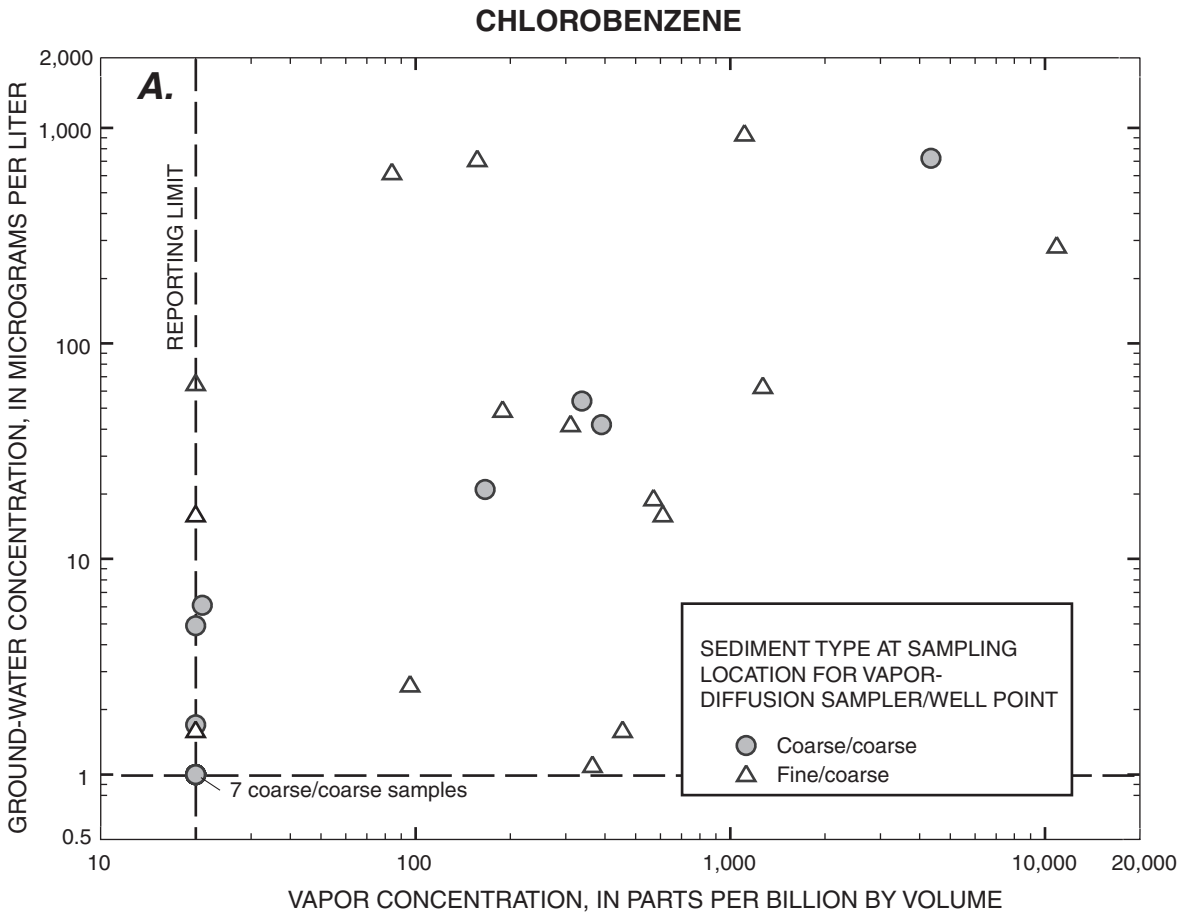


Figure 5. Concentrations of (*A*) chlorobenzene and (*B*) trichloroethylene by sediment type in ground-water and vapor samples upstream from Mill Pond, Ashland, Massachusetts.

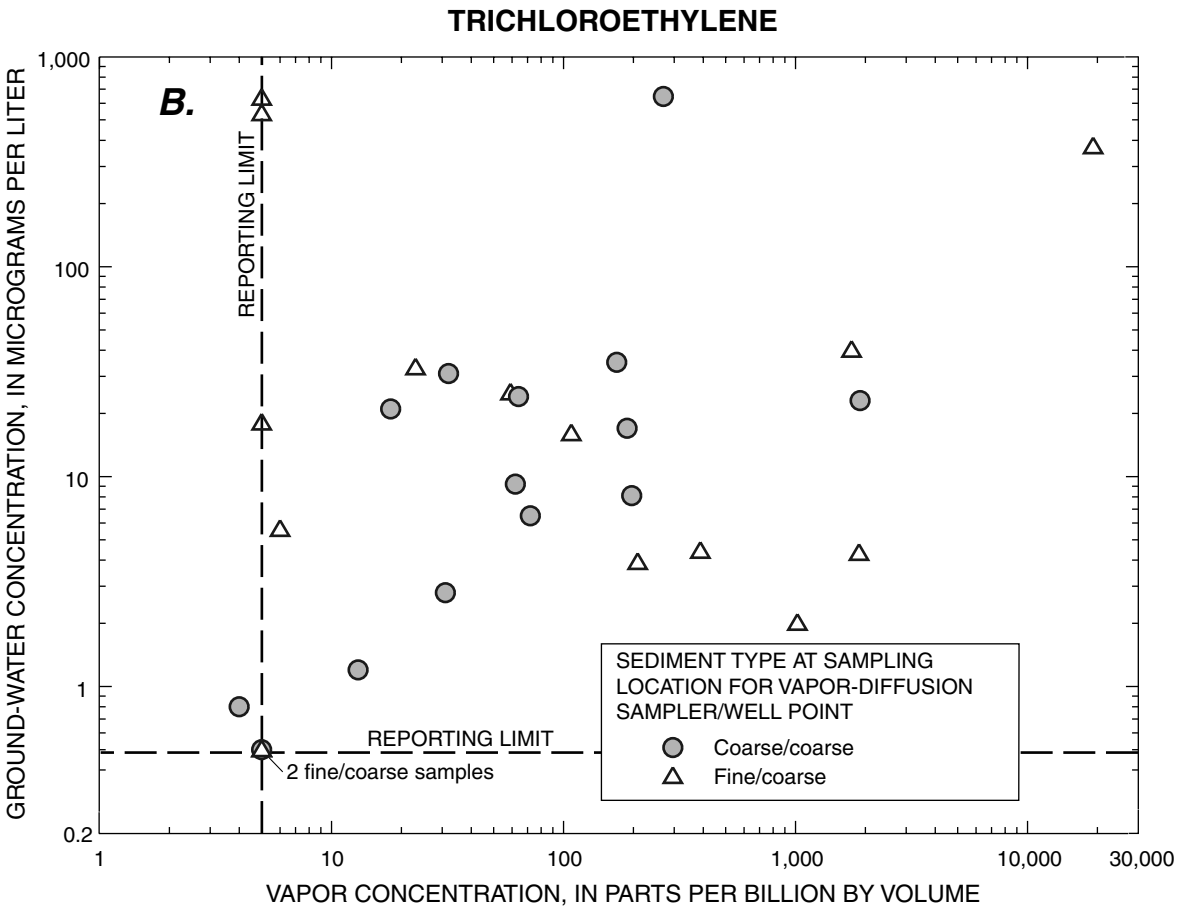


Figure 5. Concentrations of (*A*) chlorobenzene and (*B*) trichloroethylene by sediment type in ground-water and vapor samples upstream from Mill Pond, Ashland, Massachusetts—*Continued*.

Table 4. Comparison of ground-water and vapor-sample concentrations for chlorobenzene and trichloroethylene near Mill Pond, Ashland, Massachusetts

[Samples used in comparison: Sediment type at sampling location for vapor-diffusion sampler/well point. *p*-values less than 0.1000, shown in bold type, indicate a significant correlation]

Constituent	Samples used in comparison	Kendall's Tau *p*-value	Number of samples in comparison	Number of samples with concentrations less than the reporting limit	
				Ground water	Vapor
Upstream from Mill Pond					
Chlorobenzene	All samples	**0.0003**	29	7	12
Chlorobenzene	Coarse/coarse	**.0003**	14	7	9
Chlorobenzene	Fine/coarse	.4854	15	0	3
Trichloroethylene	All samples	.2063	29	3	3
Trichloroethylene	Coarse/coarse	**.0138**	14	1	1
Trichloroethylene	Fine/coarse	.8794	15	2	2
Near Mill Pond					
Chlorobenzene	All samples	**.0311**	10	2	2
Chlorobenzene	Coarse/coarse	**.0909**	6	1	1
Chlorobenzene	Fine/coarse	.1742	4	1	1
Trichloroethylene	All samples	.5312	10	1	1
Trichloroethylene	Coarse/coarse	**.0909**	6	0	1
Trichloroethylene	Fine/coarse	1.0000	4	1	0

COMPARISON OF CHEMICALS IN VAPOR AND GROUND-WATER SAMPLES

Analytical results from ground-water samples for the second study phase are reported in table 5. Because a complete data set is available for all 10 well points only on the first sampling date, September 7, 2000, these data were used for statistical analyses and discussions in this section. A comparison of chlorobenzene concentrations indicates detectable concentrations generally were at the same sample locations for both vapor and ground-water samples (table 5, fig. 6*A*). Vapor concentrations for chlorobenzene in parts per billion by volume are lower or similar to ground-water concentrations in micrograms per liter at the three sample locations upstream from Mill Pond and at the upstream reference area. High concentrations of TCE in vapor and ground water were observed at the Sudbury River sampling location (SR-004) (table 5, fig. 6*B*). TCE vapor concentrations were less than ground-water concentrations at two locations upstream from Mill Pond and in the upstream reference area.

Kendall's Tau was used to compare ground-water concentrations of benzene, chlorobenzene, and TCE to ground water VOCs, SVOCs, and metals concentrations (table 6). Where the ground-water concentrations were significantly correlated to one of the constituents of interest, the constituent then was compared with vapor concentrations of benzene, chlorobenzene, and TCE. The constituents listed on table 6 include compounds that correlated significantly with benzene, chlorobenzene, and TCE in ground water. Correlations also were observed among one or all of the following constituents: ground-water benzene, chlorobenzene, or TCE, and aniline, chromium, mercury, nitrobenzene, selenium, silver, 1,2,4-trichlorobenzene, and vanadium. Because no relation was found between these constituents and vapor concentrations of benzene, chlorobenzene, or TCE, the constituents are not included in the table.

Table 5. Concentration of selected contaminants from ground-water and vapor samples at 10 well points near Mill Pond, Ashland, Massachusetts

[Sample locations are shown on figure 1. Data for water samples from R.F. Weston, Inc., 2001. **Sample type:** W, water-sample concentration in micrograms per liter, samples collected on September 7, 2000; V, vapor-sample concentration in parts per billion by volume, samples collected on September 12, 2000. Contaminant not detected at the reporting limit in parentheses]

Contaminant	Sample type	Sample location									
		UR-001	MP-03A-3	MP-004-2	MP-007-1	SR-003	SR-004	SR-008	RW-008	RW-009	RW-010
Volatile organic compound											
Benzene	W	(1.0)	(94)	(83)	(2.9)	(1.0)	(40)	[1]4.3	(1.0)	21	33
	V	(15)	60	76	(15)	(15)	200	(15)	(15)	300	980
Chlorobenzene	W	13	1,200	1,100	(2.9)	(1.0)	1,000	130	28	130	530
	V	(100)	1,200	430	(280)	130	7,800	390	1,000	1,600	4,700
Chloroform	W	(1.0)	(94)	(83)	(2.9)	(1.0)	(40)	(6.6)	1.1	(8.3)	[1]12
cis-1,2-Dichloroethene	W	9.3	900	2,300	(2.9)	(1.0)	72	[1]4.9	1.4	39	140
1,2-Dichloroethene (total)	W	9.8	940	2,400	(2.9)	(1.0)	76	[1]5.1	1.5	41	150
Methylene chloride	W	(1.0)	140	110	(2.9)	(1.0)	(40)	9.1	(1.0)	(8.3)	(24)
Trichloroethylene	W	25	2,400	430	(2.9)	[1]0.76	780	180	13	220	620
	V	(14)	[1]11	26	380	95	11,000	950	1,100	6,100	2,400
Semi-volatile organic compound											
1,2-Dichlorobenzene	W	(10)	1,100	1,100	58	(10)	420	13	(10)	110	270
1,4-Dichlorobenzene	W	(10)	230	230	12	(10)	72	[1]3.4	(10)	18	39
Metals											
Beryllium	W	0.34	8.1	9.5	1.6	(0.1)	12.9	4.0	1.1	3.2	1.9
Calcium	W	7,830	155,000	151,000	35,200	15,800	174,000	96,100	22,900	56,300	93,600
Cobalt	W	(1.3)	441	257	20.1	(1.3)	412	29.3	16.3	39.4	79.5
Iron	W	351	33,700	42,900	22,600	401	31,600	8,910	1,420	915	107,000
Magnesium	W	1,630	36,700	31,100	3,470	3,720	67,600	21,300	2,690	7,990	18,700
Manganese	W	945	30,600	32,600	5,420	190	56,300	14,000	1,040	2,320	4,560
Nickel	W	(1.6)	144	108	45.4	(1.6)	150	6.2	6.3	33.3	84.6
Potassium	W	2,090	18,000	20,400	6,630	3,410	16,400	9,660	4,650	7,730	13,900
Sodium	W	30,800	1,440,000	1,180,000	135,000	56,200	1,090,000	281,000	75,300	320,000	534,000
Zinc	W	9.9	543	63.7	18.4	13.1	438	22.7	36.9	178	8.2

[1]Contaminant detected below the practical quantitation limit.

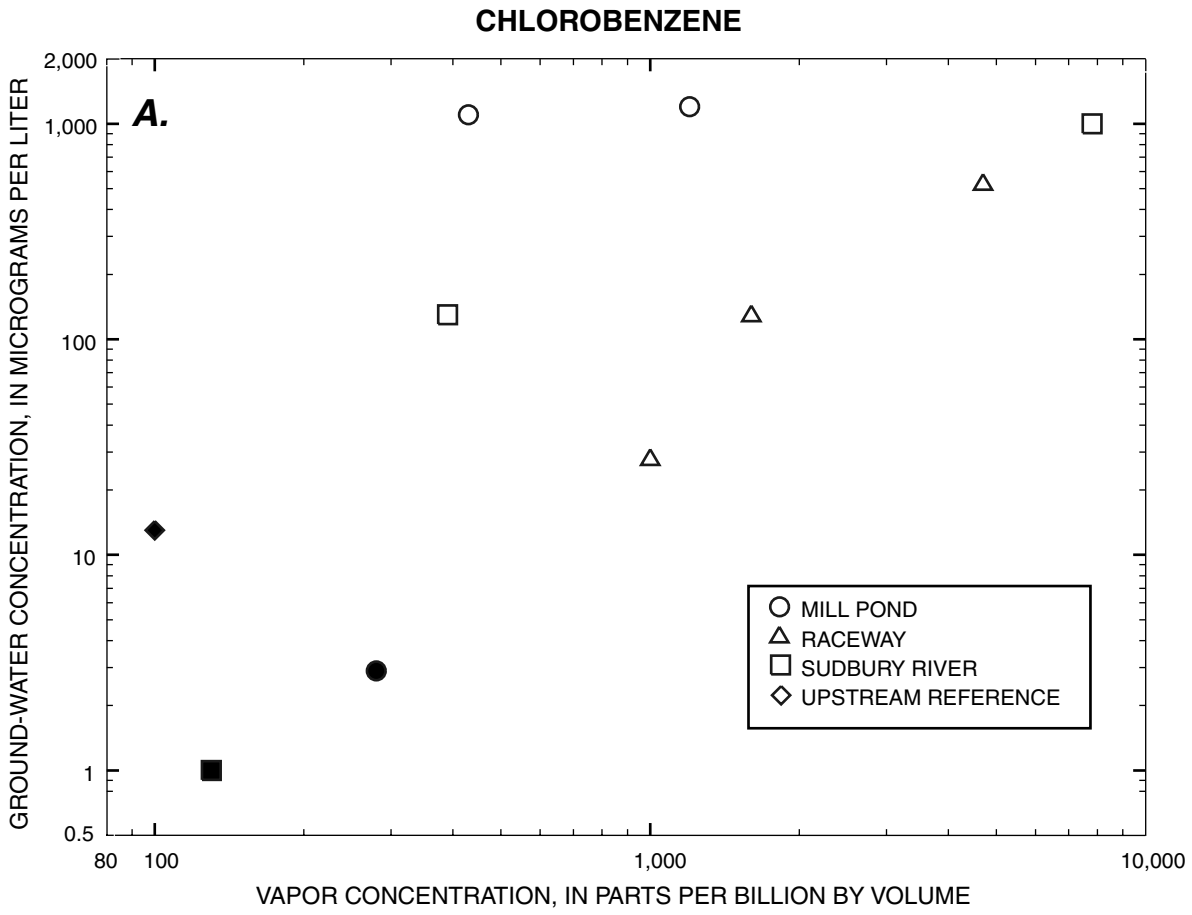


Figure 6. Concentrations of (*A*) chlorobenzene and (*B*) trichloroethylene in ground-water and vapor samples near Mill Pond, Ashland, Massachusetts. Solid symbols represent one or both concentrations at or below the reporting limit.

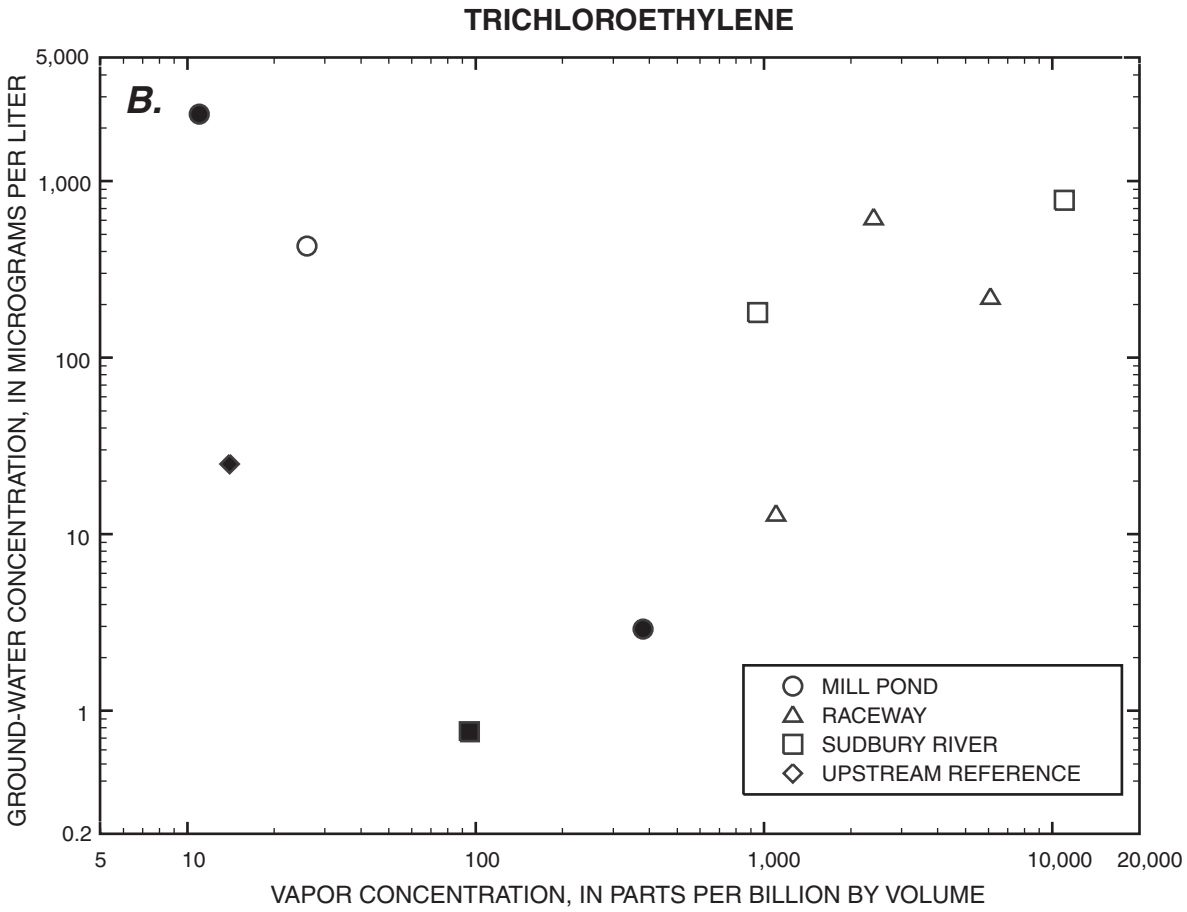


Figure 6. Concentrations of (*A*) chlorobenzene and (*B*) trichloroethylene in ground-water and vapor samples near Mill Pond, Ashland, Massachusetts. Solid symbols represent one or both concentrations at or below the reporting limit—*Continued*.

Table 6. Kendall's Tau *p*-values for selected volatile organic compounds in ground water and vapor compared to selected volatile organic compounds, semi-volatile organic compounds, and metals in ground water at well points near Mill Pond, Ashland, Massachusetts

[*p*-values less than 0.1000, shown in bold type, indicate a significant correlation; NA, not applicable; sample size is 10]

Constituent in ground water	Ground water			Vapor		
	Benzene	Chloro-benzene	Trichloro-ethylene	Benzene	Chloro-benzene	Trichloro-ethylene
Volatile organic compound						
Benzene	NA	**0.0007**	**0.0020**	**0.0977**	**0.0293**	0.7165
Chlorobenzene	**0.0007**	NA	**.0006**	.1229	**.0311**	.7194
Chloroform	**.0001**	**.0004**	**.0023**	.1012	**.0196**	.5900
cis-1,2-Dichloroethene	**.0020**	**.0023**	**.0032**	**.0436**	.1797	.9287
1,2-Dichloroethene (total)	**.0020**	**.0023**	**.0032**	**.0436**	.1797	.9287
Methylene chloride	**.0002**	**.0007**	**.0037**	.1440	**.0458**	.8559
Trichloroethylene	**.0020**	**.0006**	NA	**.0436**	**.0157**	.5312
Semi-volatile organic compound						
1,2-Dichlorobenzene	**.0003**	**.0019**	**.0047**	**.0784**	**.0556**	.7845
1,4-Dichlorobenzene	**.0023**	**.0104**	**.0227**	**.0784**	**.0833**	.9274
Metals						
Beryllium	**.0065**	**.0071**	**.0157**	.1024	**.0603**	.4208
Calcium	**.0002**	**.0041**	**.0095**	.1024	**.0157**	.5312
Cobalt	**.0003**	**.0009**	**.0012**	**.0669**	**.0119**	.4725
Iron	**.0183**	**.0311**	**.0603**	**.0679**	**.0892**	.7884
Magnesium	**.0037**	**.0119**	**.0253**	.1024	**.0397**	.7884
Manganese	**.0110**	**.0119**	**.0253**	.1495	**.0892**	.7884
Nickel	**.0035**	**.0089**	**.0119**	**.0669**	**.0119**	.4725
Potassium	**.0006**	**.0012**	**.0095**	.1024	**.0397**	.5312
Sodium	**.0001**	**.0006**	**.0032**	.1024	**.0157**	.5312
Zinc	**.0458**	**.0482**	**.0603**	.3872	**.0397**	.5312

Vapor concentrations of chlorobenzene appear to be strong indicators of the presence of all of the constituents shown on table 6 except for *cis*-1,2-dichloroethene and 1,2-dichloroethene (total). The relations of chlorobenzene to selected VOCs, SVOCs, and metals are shown in figures 7 to 10. Positive correlations were found for benzene vapor concentrations and 9 of the 19 constituents listed in table 6. The benzene vapor data have 8 out of 10 concentrations less than the reporting limit; therefore, these are weak correlations. TCE vapor concentrations are poor indicators of VOCs, SVOCs, and metals for all constituents analyzed. The small number of samples available for comparisons in the second study phase limit the strength of these conclusions.

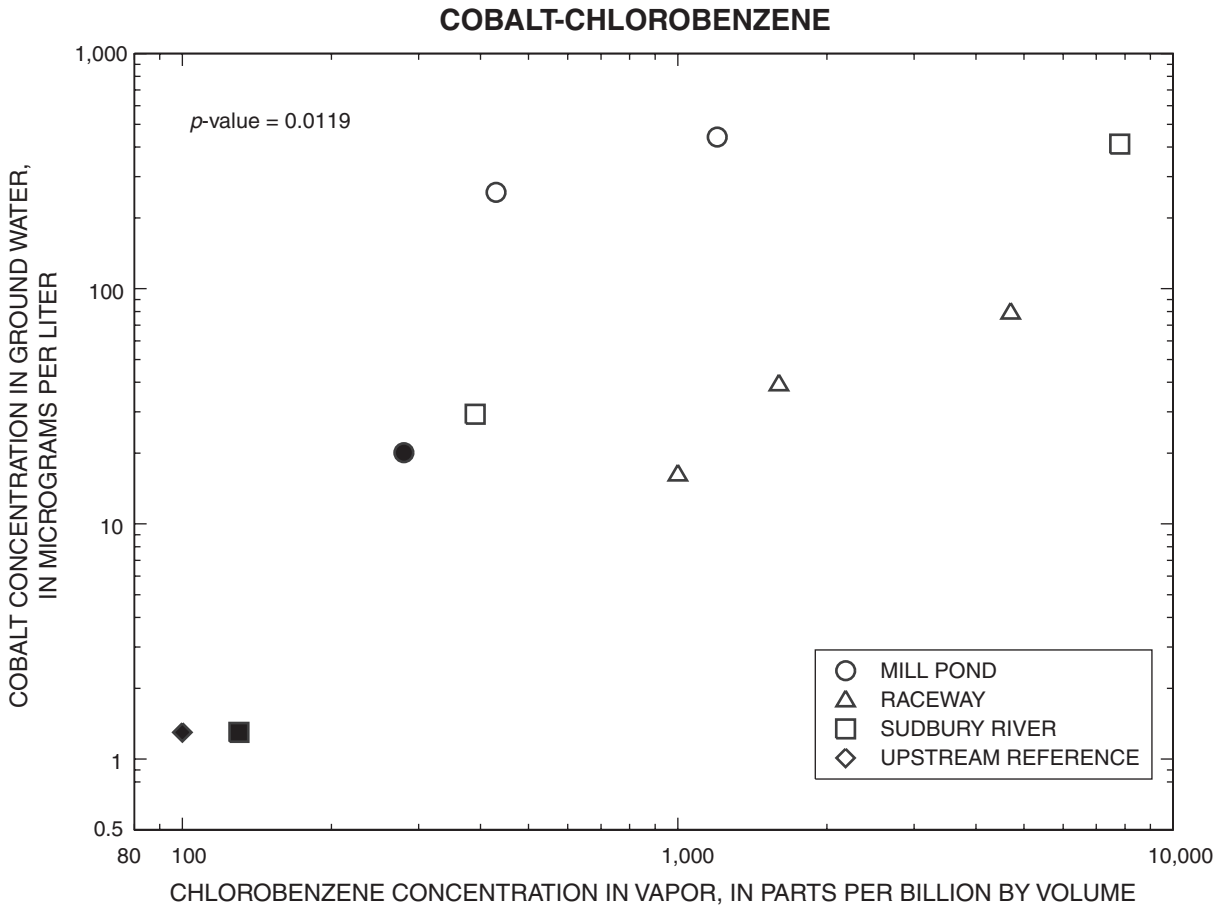


Figure 7. Cobalt concentration in ground water by chlorobenzene concentration in vapor near Mill Pond, Ashland, Massachusetts. Solid symbols represent one or both concentrations at or below the reporting limit.

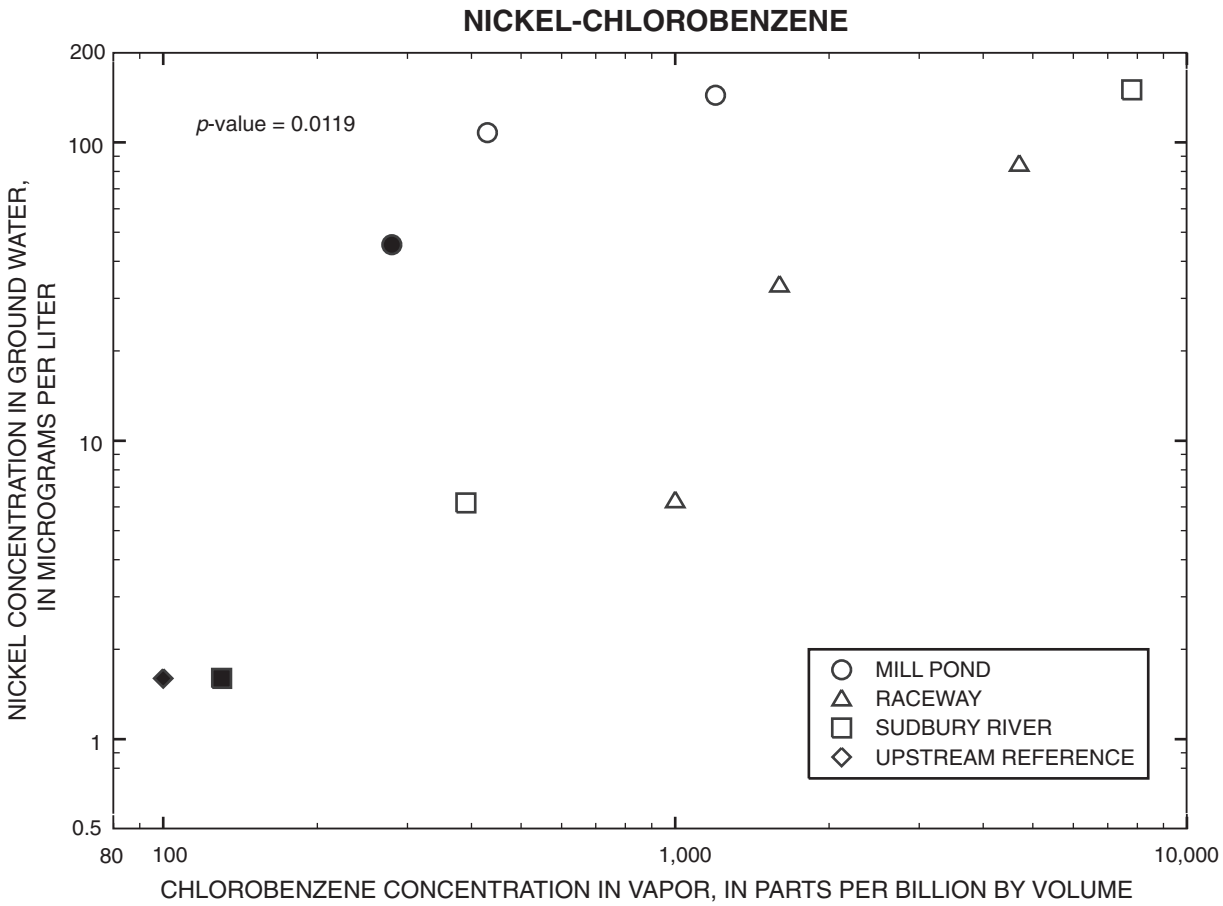


Figure 8. Nickel concentration in ground water by chlorobenzene concentration in vapor near Mill Pond, Ashland, Massachusetts. Solid symbols represent one or both concentrations at or below the reporting limit.

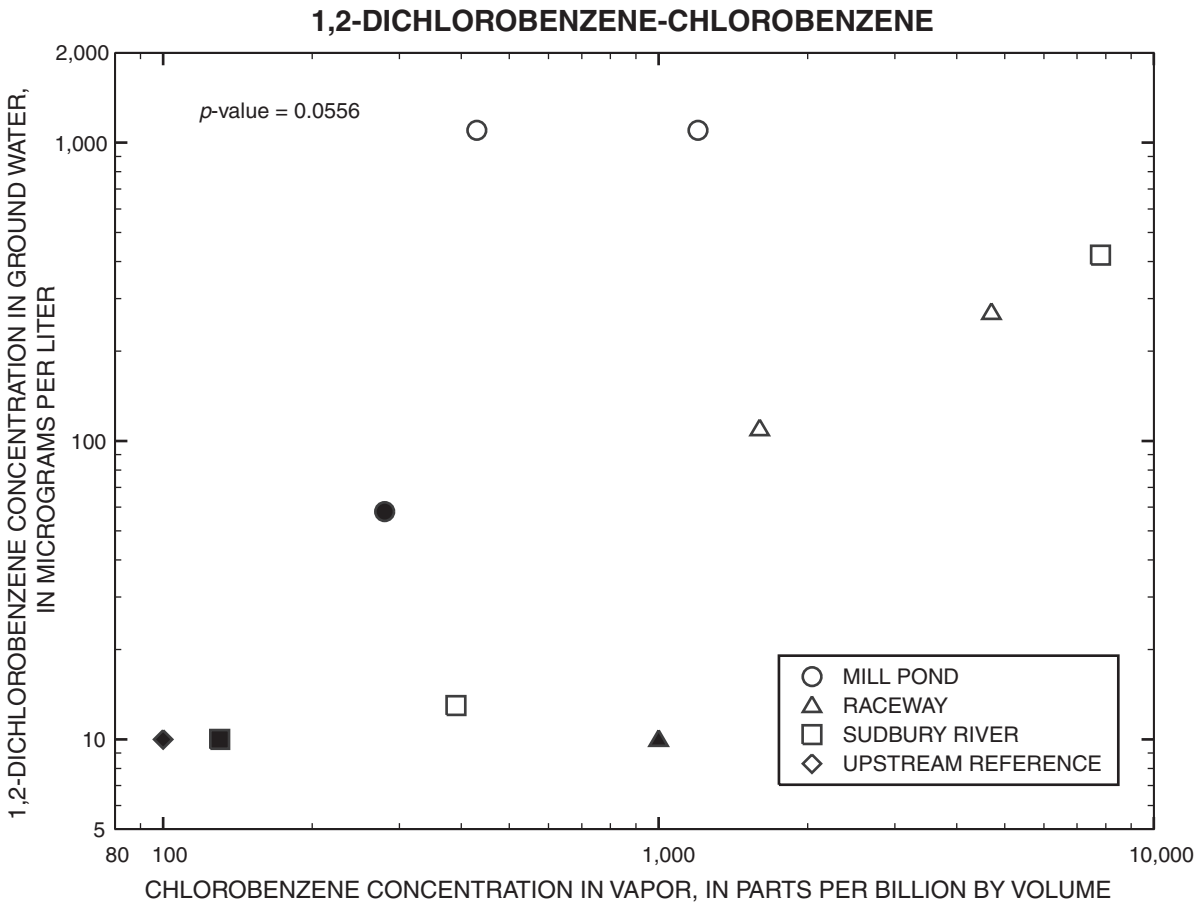


Figure 9. 1,2-dichlorobenzene concentration in ground water by chlorobenzene concentration in vapor near Mill Pond, Ashland, Massachusetts. Solid symbols represent one or both concentrations at or below the reporting limit.

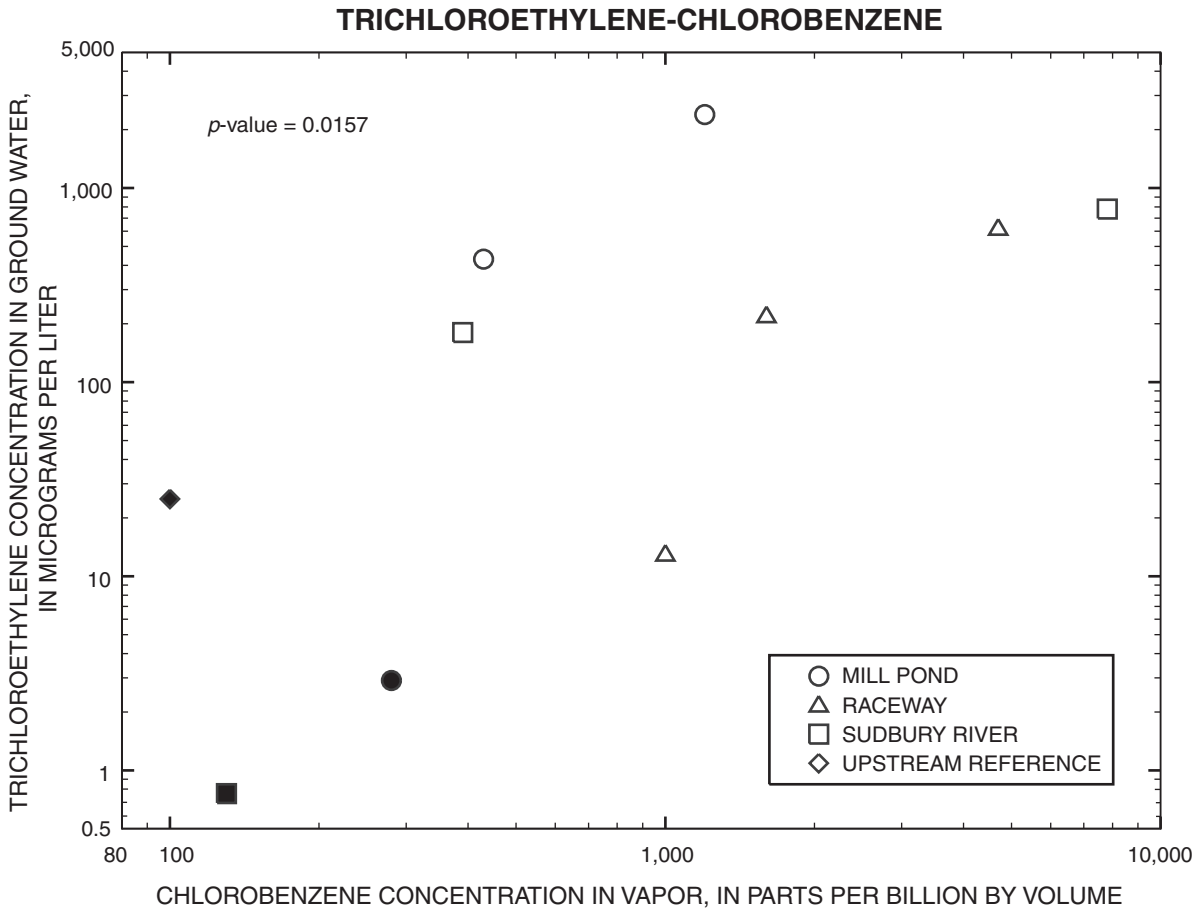


Figure 10. Trichloroethylene concentration in ground water by chlorobenzene concentration in vapor near Mill Pond, Ashland, Massachusetts. Solid symbols represent one or both concentrations at or below the reporting limit.

ASSESSMENT OF SAMPLING METHODS

Well points and PVD samplers are two reconnaissance methods for identifying areas of contamination. The time and cost involved in data collection, and the reliability of results, are factors investigators consider when selecting a method to use for a study. For this study, about 60 samplers for the first study phase were constructed by one person in about 1 day. PVD samplers were installed at 50 locations by two people in 3 days, and these samplers were retrieved by two people in 2 days; this totalled about 11 work-days or 88 hours for data collection. Forty well points were installed and sampled upstream from Mill Pond by four people in 5 days, which totalled about 20 work-days or 160 hours. The time spent on well-point installation also included taking core samples to describe sediments, and measuring other physical and chemical parameters in the field. Data-collection expenses included an equipment usage fee for a row boat and canoe for PVD sampling and a barge rental fee for well-point installation and sampling. Expenses incurred by future studies may vary depending on field conditions and available equipment.

The PVD samplers generally were installed in less than 5 minutes in sediments beneath shallow water (less than 3 ft). To install the samplers in sediments beneath deep water (3 to 5 ft) required additional time to anchor the boat and drive down the pipe-installation assembly. Because of the set-up time, the PVD samplers may require about as much time to install in deep water as the well points. About 10 percent of the PVD samplers were lost prior to or during recovery, which is higher than experienced at other sites because some samplers were destroyed by vandals. Typically, 5 percent or less of the samplers are lost prior to or during recovery.

An assessment of the quality of the data collected by the two methods is subjective. When PVD samplers and well points were installed in coarse sediments, both methods yielded similar results and both methods reliably map VOC distribution. VOC concentrations detected in fine sediments did not correlate with concentrations in water samples collected in coarse sediments below the fine sediments. VOC concentrations detected with PVD samplers may better reflect the concentrations in shallow, biologically active sediments than concentrations in water from well points beneath these sediments. Many factors may have affected concentrations observed in vapor samples relative to water from well points and include the following.

- Insufficient time for full equilibration of vapor with pore water. Tests of equilibration times in the study area reported by Lyford and others (1999) indicated that equilibration time may exceed 3 weeks in some instances.

- Variations in temperature between sampling sites that affected equilibrium vapor concentrations but not ground-water concentrations.
- Imprecise sampling and analytical methods. Duplicate vapor samples yielded appreciably different concentrations in some instances (table 2).
- Chemical transformations. Chemicals in ground water that move up to the stream may undergo chemical transformations in the organic-rich, presumably anoxic, fine sediments.
- Changes in concentrations with time. Because of relatively slow travel time through the fine sediments, the concentrations observed in shallow fine sediments may reflect earlier changing concentrations in deeper coarse sediments.
- Lateral variations in contaminant concentrations over short distances. Because the PVD samplers and well points were not precisely collocated, lateral variations in water quality over a distance of about 5 ft may have contributed to the lack of correlation between the two methods. Also, purging of the wells prior to sample collection may have resulted in a larger area sampled in wells than in PVD samplers.
- Mixing of surface water and ground water. Surface water can recharge shallow sediments locally (Conant, 2001) and mix with discharging ground water.
- Different flow paths intercepted. Flow paths intercepted at shallow depths may be from a more shallow part of the plume than flow paths intercepted at greater depths. The concentration of VOCs could be higher or lower at shallow depths than at greater depths, depending on the concentration profile in the plume at the river's edge.

SUMMARY AND CONCLUSIONS

A mixed plume of contaminants that includes VOCs, SVOCs, and metals in ground water near the former Nyanza, Inc., property in Ashland, Mass., discharges to the Sudbury River. This study by the U.S. Geological Survey in cooperation with the U.S. Environmental Protection Agency, designed to compare chemical analytical results from PVD samplers and well points at similar locations near Mill Pond in Ashland, Mass., also provided useful information about the distribution of VOCs in river-bottom sediments. TCE and chlorobenzene were detected in vapor samples along the northern and southern banks of an approximately 400-ft reach of the Sudbury River upstream from Mill Pond. Prior to this study, VOCs in sediment pore water were not expected to extend to the northern bank of the river.

TCE was detected in vapor and ground-water samples for a distance of 1,500 ft upstream from the entrance to Mill Pond, which is upstream from the previously mapped plume in ground water. The upstream extent of TCE in sediment pore water was not defined during this study. The extent of chlorobenzene in river sediments appears to be limited to a river reach of about 1,200 ft based on data from PVD samplers and well points, and correlates approximately with the mapped plume in ground water.

A statistical correlation was not observed between vapor and ground-water VOC concentrations for the first study phase when all collocated samples were included in the analysis. However, Kendall's Tau indicates significant correlations between vapor and ground-water concentrations for TCE and chlorobenzene upstream from Mill Pond where both sampler types are installed in coarse sediments or where the fine organic layer separating the two sampling locations is 1 ft or less.

Chlorobenzene vapor concentrations from samples collected for the second study phase correlated significantly with concentrations of 5 VOCs, 2 SVOCs, and 10 metals in water from well points. Vapor concentrations for benzene correlated significantly with 4 VOCs, 2 SVOCs, and 3 metals; but the benzene vapor data have 8 out of 10 concentrations less than the reporting limit, so these correlations are weaker than for chlorobenzene. TCE vapor concentrations did not correlate with any of the ground-water constituents analyzed for this study. Chlorobenzene vapor concentrations detected with PVD samplers appear to be strong indicators of the presence of selected VOCs, SVOCs, and metals in ground water from well points.

Many factors may have caused variability in contaminant concentrations that affected statistical comparison of the sampling methods. These factors include insufficient time for full equilibration of vapor with pore water; variations in temperature between sampling sites at the depths of PVD samplers; imprecise sampling and analytical methods; different ground-water flow paths for different sediment types and different

depths sampled; chemical transformations in the organic-rich fine sediments; changes in concentrations and ground-water flow pathways with time; and lateral variations in contaminant concentrations over distances of about 5 ft. In general, the study indicated that VOC concentrations measured in PVD samplers may be useful for identifying levels of contamination by VOCs, SVOCs, and metals where a mixed plume in ground water is the source of contaminants. Definitive results will require a larger number of vapor and water samples collected at the same depths and a study design that minimizes the sources of variability between data-collection methods.

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