U.S. Department of the Interior
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Field Tests of Polyethylene-Membrane Diffusion Samplers for Characterizing Volatile Organic Compounds in Stream-Bottom Sediments, Nyanza Chemical Waste Dump Superfund Site, Ashland, Massachusetts

Water-Resources Investigations Report 00-4108

Prepared in cooperation with the
U.S. ENVIRONMENTAL PROTECTION AGENCY

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By FOREST P. LYFORD, RICHARD E. WILLEY, and SCOTT CLIFFORD

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Northborough, Massachusetts
2000

U.S. DEPARTMENT OF THE INTERIOR
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CONVERSION FACTORS

Multiply	By	To obtain
feet (ft)	0.3048	meters
inches (in.)	2.54	centimeters
mil (mil)	0.0254	millimeters

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

°F=1.8 °C+32

VERTICAL DATUM

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

ABBREVIATIONS

cis-DCE	cis-1,2-dichloroethene
ppb v	parts per billion by volume
mg/kg	milligrams per kilogram
mL	milliliter
PCE	tetrachloroethene
SVOCs	semi-volatile organic compounds
TCE	trichloroethene
µg/kg	micrograms per kilogram
µg/L	micrograms per liter
µS/cm	microsiemens per centimeter at 25°C
VOCs	volatile organic compounds

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By Forest P. Lyford, Richard E. Willey, *and* Scott Clifford

Abstract

A plume of volatile organic compounds (VOCs) in ground water extends from the Nyanza Chemical Waste Dump Superfund site in Ashland, Massachusetts, northward toward a mill pond on the Sudbury River and eastward toward the Sudbury River and former mill raceway downstream from the mill pond. Polyethylene-membrane water-to-vapor (vapor) and water-to-water (water) diffusion samplers were installed in January 1999 in bottom sediments along the Sudbury River and former mill raceway in a pilot study to determine if vapor samplers would be useful in this setting for delineating a plume of contaminants in ground water near the river and raceway, to evaluate equilibration time for vapor-diffusion samplers, and to determine if diffusion samplers might be an alternative to seepage meters (inverted steel drums) and sediment sampling for evaluating concentrations of VOCs in bottom sediments.

Of five tested compounds (benzene, trichloroethene, toluene, tetrachloroethene, and chlorobenzene), chlorobenzene and trichloroethene were most frequently detected in vapor from vapor-diffusion samplers. The distribution of VOCs was generally consistent with a previously mapped plume of contaminants in ground water. The field evaluation of equilibration times for vapor-diffusion samplers was inconclusive because of changing hydrologic conditions that may have affected concentrations of VOCs, possible variations in concentrations of VOCs over short distances, and imprecise sampling and analytical methods. The limited data, however, indicated that equilibration may require 3 weeks or more in some settings.

VOCs detected in samples from water-diffusion samplers and their concentrations were comparable to results from seepage meters, and VOCs detected in vapor-diffusion samplers correlated with VOCs detected in water-diffusion samplers. These results indicate that either vapor- or water-diffusion samplers would serve as an economical alternative to seepage meters for sampling of VOCs in pore water from stream-bottom sediments. Results from diffusion samplers correlated poorly with results from sediment samples, partly because of high quantitation limits for chemical analyses of sediments. In general, results from the diffusion samplers better represented the distribution of VOCs than the results from the sediment samples. This pilot study indicates that diffusion samplers are an economical means of identifying "hot spots" for contaminants in bottom sediments and can provide insights on transport pathways for contaminants near surface-water bodies. After establishing equilibration times for a particular site, diffusion samplers also may be useful for studying variations in concentrations of VOCs over short distances, variations with time and changing hydrologic conditions, and processes such as chemical transformations by biodegradation and exchanges between surface water and ground water in the hyporheic zone.

INTRODUCTION

Volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) are present in ground water near the Nyanza Chemical Waste Dump Superfund site (Nyanza site) in Ashland, Mass. (Roy F. Weston, Inc., 1998). Water-quality data and water-level data from monitoring wells indicate that contaminated ground water discharges to the surface in two areas: (1) along the Sudbury River at the upstream end of a mill pond and (2) along the Sudbury River and a former mill raceway downstream from the mill pond and parallel to the river (fig. 1) (Roy F. Weston, Inc., 1998). During 1998–99, the U.S. Environmental Protection Agency (USEPA), through the U.S. Army Corps of Engineers (USACE), supported a study by Roy F. Weston, Inc. (1999b) of contaminants in bottom sediments along the Sudbury River and former mill raceway. In this study, water was extracted from inverted steel drums (seepage meters) placed in stream-bottom sediments. Bottom sediments also were sampled for VOCs, SVOCs, and mercury. The USEPA requested that the USGS use polyethylene-membrane water-to-vapor diffusion samplers (referred to as vapor-diffusion samplers in this report) to test their application for delineating the distribution of VOCs in ground-water discharge areas and as a pilot study to determine if vapor- and polyethylene-membrane water-to-water-diffusion samplers (referred to as water-diffusion samplers in this report) might serve as cost-effective alternatives to other methods for characterizing contaminants at the interface between ground water and surface water. Also of interest to USEPA is the time needed for VOC concentrations in ground water to re-equilibrate after sediments have been disturbed by emplacement of vapor-diffusion samplers.

The objectives of this study were to:

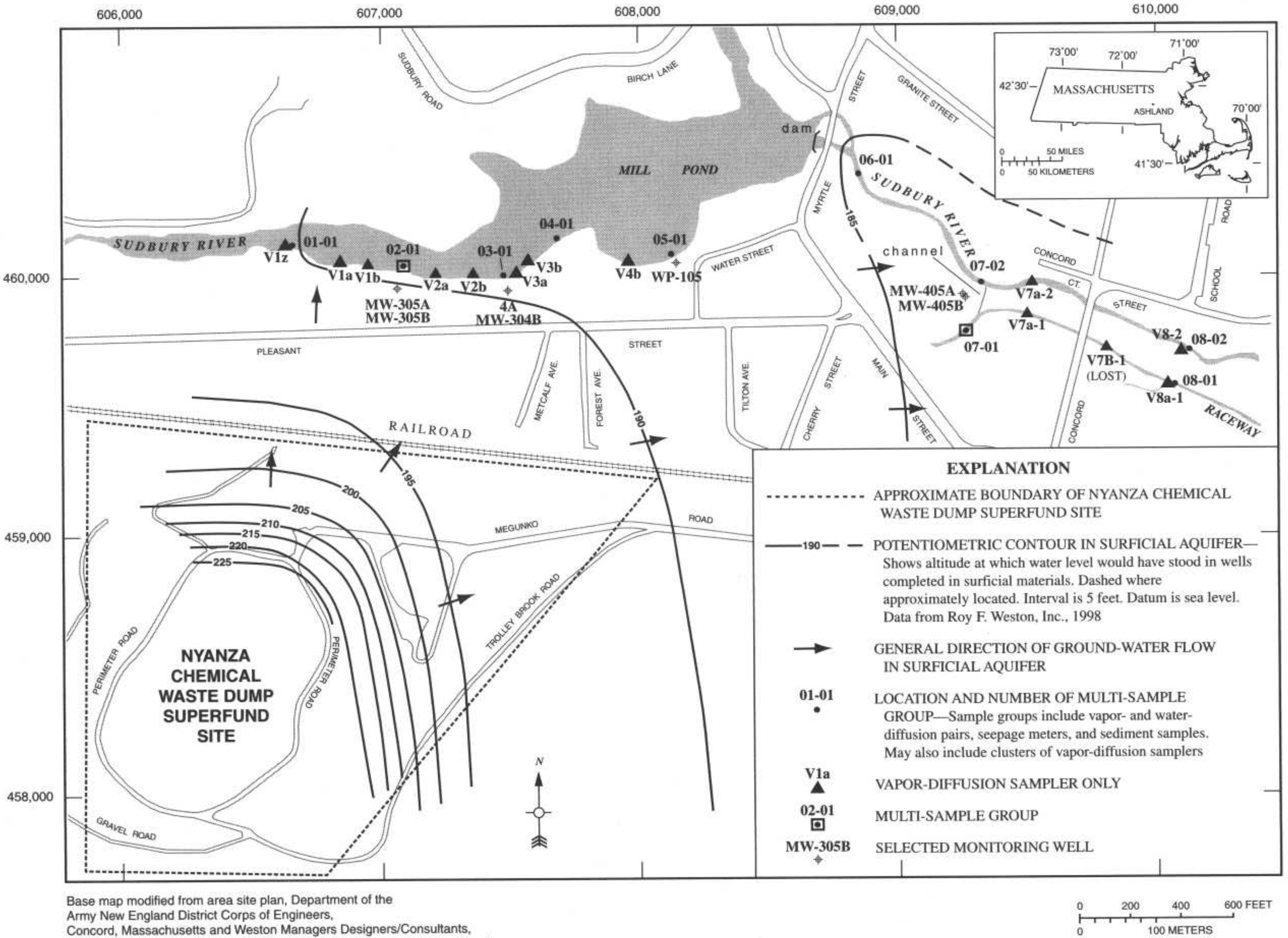
1. Determine if the distribution and concentrations of VOCs detected in vapor-diffusion samplers, which were placed in stream-bottom sediments, are consistent with the previously mapped distribution of contaminants in ground water near the Nyanza site, Ashland, Mass.
2. Determine the time needed for VOCs in bottom sediments to re-equilibrate after installation of the samplers.
3. Determine if vapor- and water-diffusion samplers might serve as alternatives to other sampling techniques, specifically seepage meters and sediment sampling, to characterize the occurrence of VOCs in stream-bottom sediments.

This report (1) describes the distribution of VOCs along the Sudbury River and mill raceway determined by use of vapor-diffusion samplers; (2) presents results of an experiment to determine equilibration times for VOCs after installation of samplers in sediments; (3) compares results from vapor-diffusion samplers to results from water-diffusion samplers, seepage meters, and sediment sampling; (4) discusses considerations for using diffusion samplers on the basis of results from this pilot study, and suggests additional studies that would further test and refine the use of diffusion samplers for characterizing contaminants at the interface between ground water and surface water.

USGS personnel constructed, installed, and retrieved vapor and water-diffusion samplers. The vapor-diffusion samples were analyzed on site by Scott Clifford, USEPA. Water samples from diffusion samplers and water samples from seepage meters were submitted by Roy F. Weston, Inc., personnel to a private laboratory for analysis. Appreciation is extended to Sharon Hayes, USEPA Site Manager, and Kathleen Taylor, Roy F. Weston, Inc., for logistical support and assistance during the study.

DESCRIPTION OF STUDY AREA

The study area is along the Sudbury River in Ashland, Massachusetts. At its closest point, the river is approximately 700 ft north of the Nyanza site (fig. 1). The upstream part of the study area is within a former mill pond. The downstream part of the study area below the mill pond includes the Sudbury River and a former mill raceway.



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 Nyanza Chemical Waste Dump Superfund Site, sampling locations, potentiometric-surface contours for the surficial aquifer, and directions of ground-water flow, Ashland, Massachusetts.

The ground-water system includes a surficial aquifer that consists of glacial lake deposits, till, and fractured crystalline rock. The glacial lake deposits range in grain size from silt to coarse sand and gravel. The thickness of fine-grained sediments increases eastward, and the till layer is discontinuous beneath the lake sediments (Ebasco Services, Inc., 1991, figs. 3–5 to 3–12). The depth to bedrock increases from less than 30 ft in the mill pond area to nearly 80 ft in an east-west trending trough that passes through the area near wells MW-405A and MW-405B downstream from the dam (Ebasco Services, Inc., 1991, fig. 3-1) (fig. 1). Most of the Superfund Site is on till-covered bedrock.

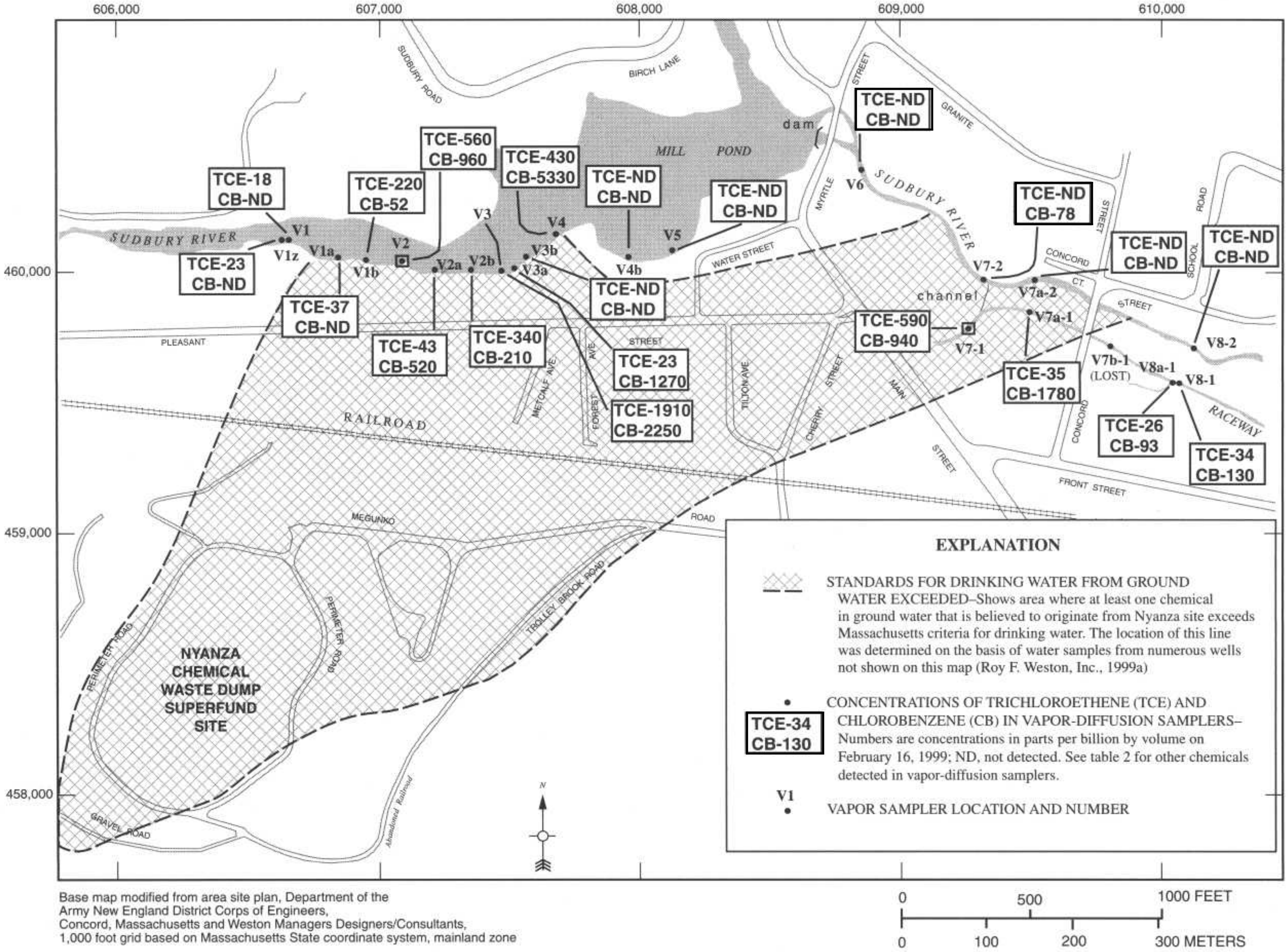
In general, ground water flows northward and eastward from the Nyanza site toward the Sudbury River. A potentiometric surface map for the surficial aquifer (Roy F. Weston, Inc., 1998) (fig. 1) indicates that ground water in the western part of the study area flows northward toward the Sudbury River at the upstream end of the mill pond. The close spacing of potentiometric contours within the Nyanza site reflects the occurrence of ground water in poorly transmissive till. The direction of ground-water flow shifts eastward near the downstream end of the mill pond and downstream from the mill pond. Water-level data presented by Roy F. Weston, Inc. (1998), also indicate that water infiltrates from the pond to the aquifer downstream from sampling location 04-01. The raceway appears to receive much of its water from ground-water sources. During the study period, however, the upstream end of the raceway was receiving some flow from the Sudbury River through a connecting channel (fig. 1).

A plume of contaminants in the surficial and bedrock aquifer system extends from the area of the Nyanza site northward to the Sudbury River and mill pond. The plume also extends eastward to the river and raceway downstream from the dam (fig. 2). VOCs that have been detected in ground water include 1,1,1-trichloroethane, benzene, chlorobenzene, cis-DCE, PCE, TCE, and vinyl chloride (Roy F. Weston, Inc., 1999a; 1999b). Chlorobenzene, TCE, and cis-DCE are the VOCs most commonly detected in ground water. Concentrations of VOCs in water from monitoring wells near the mill pond (fig. 1) are highest in well MW-305A, which was completed in bedrock. VOCs detected in a sample collected from this well in January 1999 included chlorobenzene (2,400 μg/L), cis-DCE (82 μg/L), TCE (2,700 μg/L), and vinyl chloride (2 μg/L). Also detected were mercury (1.38 μg/L) and the SVOCs 1,2,4-trichlorobenzene (71 μg/L), 1,2-dichlorobenzene (1,700 μg/L), 1,3-dichlorobenzene (69 μg/L), and 1,4-dichlorobenzene (350 μg/L). VOC concentrations in a water sample collected from well MW-305B completed in surficial materials at the same location were less than 10 μg/L, mercury concentration was 0.109 μg/L, and SVOCs were not detected.

Concentrations of VOCs in water from monitoring wells MW-405A and MW-405B located between the Sudbury River and the mill raceway are highest in well MW-405B completed in the surficial aquifer. VOCs detected in a sample collected from this well in January 1999 included chlorobenzene (5,600 μg/L), cis-DCE (120 μg/L), and TCE (7,600 μg/L). Vinyl chloride was below the detection limit of 2 μg/L. Also detected were mercury (0.0124 μg/L) and the SVOC 1,2-dichlorobenzene (450 μg/L). The SVOCs 1,3-dichlorobenzene, and 1,4-dichlorobenzene were below the detection limits of 220 μg/L. VOCs detected in a water sample collected from well MW-405A, which was completed in bedrock at the same location, were chlorobenzene (29 μg/L) and TCE (34 μg/L). Mercury was detected at a concentration of 0.0256 μg/L, and concentrations of SVOCs were below 50 μg/L.

Stream-bottom materials near sampling site 01-01 are cobbles and pebbles. Downstream from this site, the bottom material is a thick layer of soft organic matter. In the cove of the mill pond near sampling site 05-05, bottom materials along the shore are rocks and gravel. The river bottom downstream from the dam consists of rocks and coarse gravel. Bottom materials along the raceway are mainly soft and organic-rich, except near the downstream sampling location (08-01) where the bottom consists of gravel.

At the time samplers were installed on January 19–20, 1999, the mill pond was ice covered except in a few open areas near the shore. Several samplers were placed through holes cut in the ice. The river and raceway downstream from the dam were ice free. Several rain storms and periods of snowmelt caused streamflow and stream stage to rise during the period when samplers were in place. The pond was largely ice free when samplers were retrieved on February 16, 1999. Stage hydrographs for the Sudbury River at Saxonville, Mass., and the Assabet River at Maynard, Mass. (fig. 3), located several miles from Ashland, indicate that streamflow conditions varied during the study period.



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 2. The extent of contaminants in ground water and concentrations of chlorobenzene and trichloroethene detected in vapor-diffusion samplers on February 16, 1999, Ashland, Massachusetts.

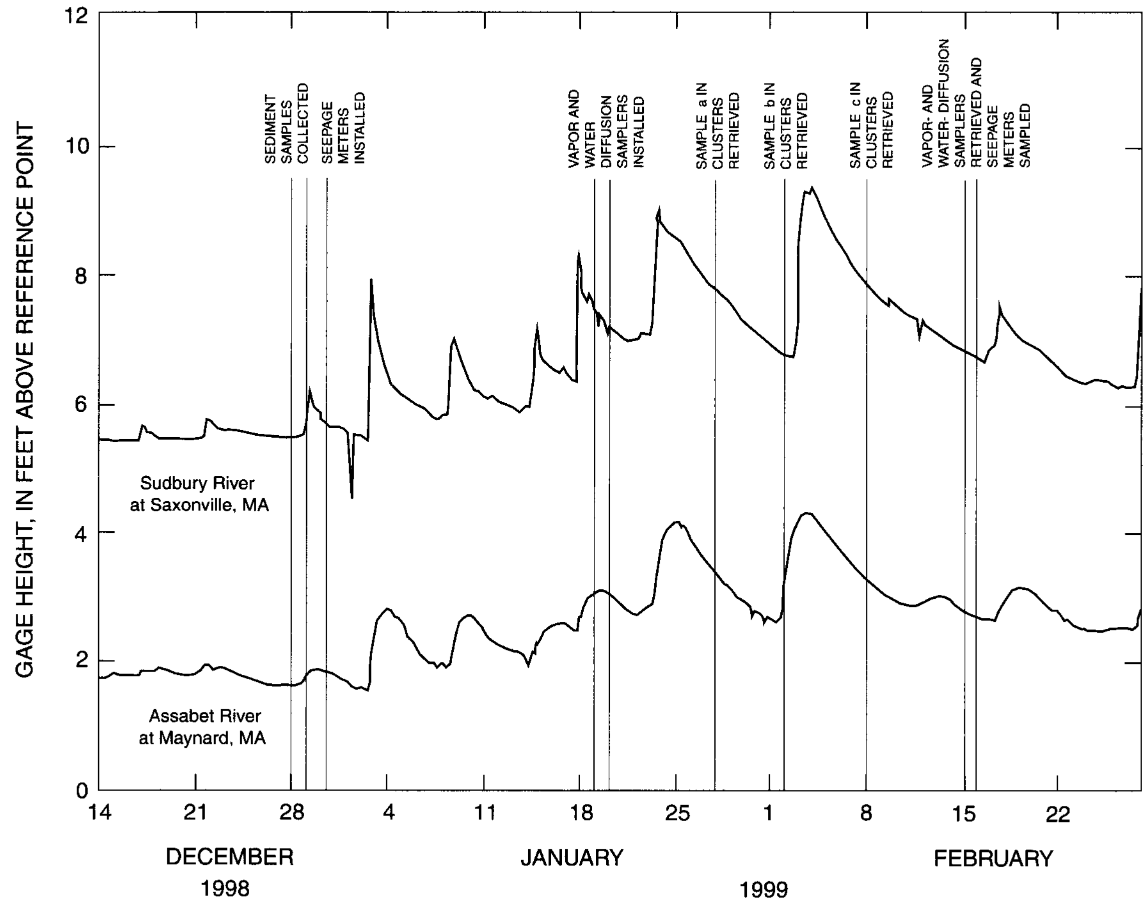


Figure 3. Stream-stage hydrograph for the Sudbury River at Saxonville, Massachusetts, and the Assabet River at Maynard, Massachusetts, and sampling dates, December 1998 to February 1999.

STUDY METHODS

Vapor- and water-diffusion samplers were constructed using methods modified slightly from those described by Vroblesky and others (1996), Vroblesky and Hyde (1997), and Vroblesky and others (1999). Vapor samplers consisted of an uncapped 40-mL, air-filled bottle inside two layers of 4-mil thick polyethylene tubing that had been secured with plastic cable ties. Upon retrieval, the outer layer of polyethylene was removed and a cap was placed on the bottle over the inner layer. Water-diffusion samplers consisted of a 4-mil thick polyethylene tube filled with deionized water and heat sealed at both ends. The tube contained enough water to fill three 40-mL vials. Table 1 summarizes sample numbers for each sample type at each location. For this report, a location may include several samplers or sampling points within a radius of about 6 feet. Sample sites and numbers are shown on figure 1.

Vapor- and water-diffusion samplers (sampler pairs) were placed together in a wire cage for protection and inserted in bottom sediments at nine locations (fig. 1) on January 19–20, 1999. The samplers were placed at a distance of 5 to 6 feet from seepage meters to minimize effects, if any, of sampler installation on operation of the seepage meters. The samplers were inserted manually into a hole formed behind a narrow-bladed shovel inserted into the bottom sediments to depths of 6 to 8 in. below the stream bottom. The vapor- and water-diffusion pair was omitted at location 08-02, but a single vapor-diffusion sampler was installed.

Two clusters of three closely spaced (within 1 foot laterally) vapor-diffusion samplers were placed near the seepage meters at each of the locations 02-01 and 07-01 to evaluate the equilibration time in two areas where concentrations of VOCs were likely to be elevated (fig. 4). The clusters were placed 5 to 6 ft from the seepage meters, and one cluster at each of the two

Table 1. Summary of sample numbers at sampling locations, Nyanza Chemical Waste Dump Superfund Site, Ashland, Massachusetts

[No., number]

Sampling location No.	Sediment sample No.	Seepage meter No.	Vapor-diffusion sample No.	Water-diffusion sample No.	Vapor-diffusion cluster No.
Sudbury River in Millpond					
01-01	SW01-01	PW01-01	V1	W1	none
02-01	SW02-01	PW02-01	V2	W2	V2-C1a, b, and c V2-C2a, b, and c
03-01	SW03-01	PW03-01	V3	W3	none
04-01	SW04-01	PW04-01	V4	W4	none
05-01	SW05-01	PW05-01	V5	W5	none
Sudbury River Downstream from Dam					
06-01	SW06-01	PW06-01	V6	W6	none
07-02	SW07-02	PW07-02	V7-2	W7-2	none
08-02	SW08-02	PW08-02	V8-2	none	none
Former Mill Raceway					
07-01	SW07-01	PW07-01	V7-1	W7-1	V7-C1a, b, and c V7-C2a, b, and c
08-01	SW08-01	PW08-01	V8-1	W8-1	none

seepage meters was at the location of the vapor- and water-diffusion pair. Clusters at location 02-01 were labeled V2-C1a, b, and c and V2-C2a, b, and c, and clusters at location 07-01 were labeled V7-C1a, b, and c and V7-C2a, b, and c (table 1, fig. 4).

Additional vapor-diffusion samplers were placed at 13 locations near and between sampling locations (fig. 1) to better define the extent of VOCs in bottom sediments. Labels for these samplers included lowercase letters a and b in downstream order from the sampling location. For example, V1a is downstream from location 01-01 and V2a is downstream from location 02-01. Vapor samplers V1z near location 01-01 and V8a-1 near location 08-01 are exceptions to this labeling scheme. Duplicate vapor-diffusion samplers were placed at four of these locations for quality assurance. A sampler (V7b-1) placed in the raceway disappeared prior to retrieval. Installation points were limited downstream from the dam on the Sudbury River because of steep banks, deep and swift water, and rocky bottom materials.

Vapor-diffusion samplers were installed with a narrow-bladed shovel as discussed above, or, in areas of deep water (generally greater than 2 ft), through a hole formed by driving a pipe assembly that consisted of a 2-inch outer pipe and a 1.5-inch, pointed inner pipe into bottom sediments. In general, samplers were at depths that ranged from 8 to 12 in. in bottom sediments. Samplers at each cluster, however, were at a uniform depth of 12 in.

One vapor-diffusion sampler from each of the 4 clusters was retrieved once a week for 3 weeks after installation and transported with a trip blank to the USEPA Lexington laboratory for analysis. The remaining vapor samplers and water-and vapor-diffusion sampler pairs were retrieved four weeks after installation when water samples were collected from seepage meters. Installation and retrieval dates are shown with stream-stage data on figure 3.

Vapor-diffusion samples were analyzed for VOCs in accordance with the Region I standard air screening method (U.S. Environmental Protection Agency, 1998) with a Photovac gas chromatograph equipped with a 4-foot by 1/8-inch SE-30 column and photoionization detector. Samples were analyzed within 3 hours of sample collection. Samples collected on February 16, 1999, were analyzed onsite in a mobile laboratory. Target compounds for vapor samples were benzene, toluene, TCE, PCE, and chlorobenzene.

Water samples were decanted from the polyethylene tubes to 40-mL glass vials that contained hydrochloric acid as a preservative. These samples were shipped with samples from the seepage meters to a contract laboratory for analysis of VOCs using USEPA Method 8260. The VOCs that were analyzed using Method 8260 are as follows:

Chloromethane
Bromomethane
Vinyl Chloride
Chloroethane
Methylene Chloride
Trichlorofluoromethane
1,1-Dichloroethylene
1,1-Dichloroethane
1,2-Dichloroethylene isomers
Chloroform
1,2-Dichloroethane
1,1,1-Trichloroethane
Carbon Tetrachloride
Bromodichloromethane
1,2-Dichloropropane
t-1,3-Dichloropropene
Trichloroethene
Dibromochloromethane
c-1,3-Dichloropropene
1,1,2-Trichloroethane
Benzene
2-Chloroethylvinyl ether
Bromoform
Tetrachloroethene
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
Toluene
Chlorobenzene
Ethylbenzene
Acetone
Carbon Disulfide
2-Butanone (MEK)
2-Hexanone
4-Methyl-2-Pentanone (MIBK)
Styrene
Xylenes (total)

Seepage meters were installed on December 31, 1998, by Roy F. Weston, Inc., personnel (Roy F. Weston, Inc., 1999b) at locations summarized in table 1. A seepage meter consisted of a section of a 55-gallon steel drum that was inserted open-end down into bottom sediments. Water samples were collected through a valve placed in the top of the steel drum. Ideally, samples would be collected in a polypropylene bag attached to the valve that filled under natural seepage conditions after surface water trapped in the drum had been fully purged. Observations of seepage rates indicated that the drums would not fully purge during the study period. To reduce the time needed for purging, the seepage meters were pumped at a slow rate on January 18, 1999, using a peristaltic pump, while temperature, pH, specific conductance, oxidation-reduction potential, and dissolved oxygen were monitored to detect the possible breakthrough of surface water. Results from purging on January 18, 1999, were used to determine optimum pumping rates during sampling. Samples were collected from the seepage meters on February 15 and 16, 1999, by purging with a peristaltic pump at a rate of less than 300 mL/min. Again, the field parameters listed above were monitored to detect the possible breakthrough of surface water; the breakthrough of surface water was not apparent during sampling (Roy F. Weston, Inc., 1999b).

Sediment samples collected from the river, mill pond, and river and mill raceway by Roy F. Weston, Inc., personnel from December 26 to 30, 1998, were analyzed for mercury, arsenic, SVOCs, VOCs, and grain size (Roy F. Weston, Inc., 1999b). A number of these samples were collected at locations other than those shown on figure 1 and are not discussed in this report. All samples were collected at depths of 0 to 6 in. Sample numbers are consistent with numbers used for other sampling methods. For example, sediment sample SD01-01 is at location 01-01 (table 1).

DISTRIBUTION OF VOCS DETECTED IN VAPOR-DIFFUSION SAMPLERS

In general, the distribution of VOCs detected in vapor-diffusion samplers collected on February 16, 1999, is consistent with the mapped distribution of contaminants in ground water that exceed Massachusetts criteria for drinking water (fig. 2). Chlorobenzene and TCE were the principal VOCs detected in vapor-diffusion samplers (table 2). Either chlorobenzene, TCE, or both were detected at 10 of 13 samplers upstream from the dam (not including duplicate samples), 1 of 4 samplers along the Sudbury River downstream from the dam, and 4 of 4 samplers along the raceway. Chlorobenzene and TCE typically were detected in the same samples, except at V1, V1z and V1a where TCE was detected but not chlorobenzene and at V7-2 where chlorobenzene was detected but not TCE. Benzene was detected at five samplers (V4, V7-1, V7a-1, and V8-1, V8a-1), toluene was detected at a trace concentration in sampler V4b, and cis-DCE was identified at several samplers, but concentrations were not determined. TCE detections at location 01-01 were somewhat upstream from the mapped plume. The absence of chlorobenzene and TCE at samplers V4b and V5 at the downstream end of the mill pond is consistent with observations that the pond is a recharge source to ground water in that area. The absence of VOCs at sampler V3b cannot be explained on the basis of current knowledge about ground-water pathways.

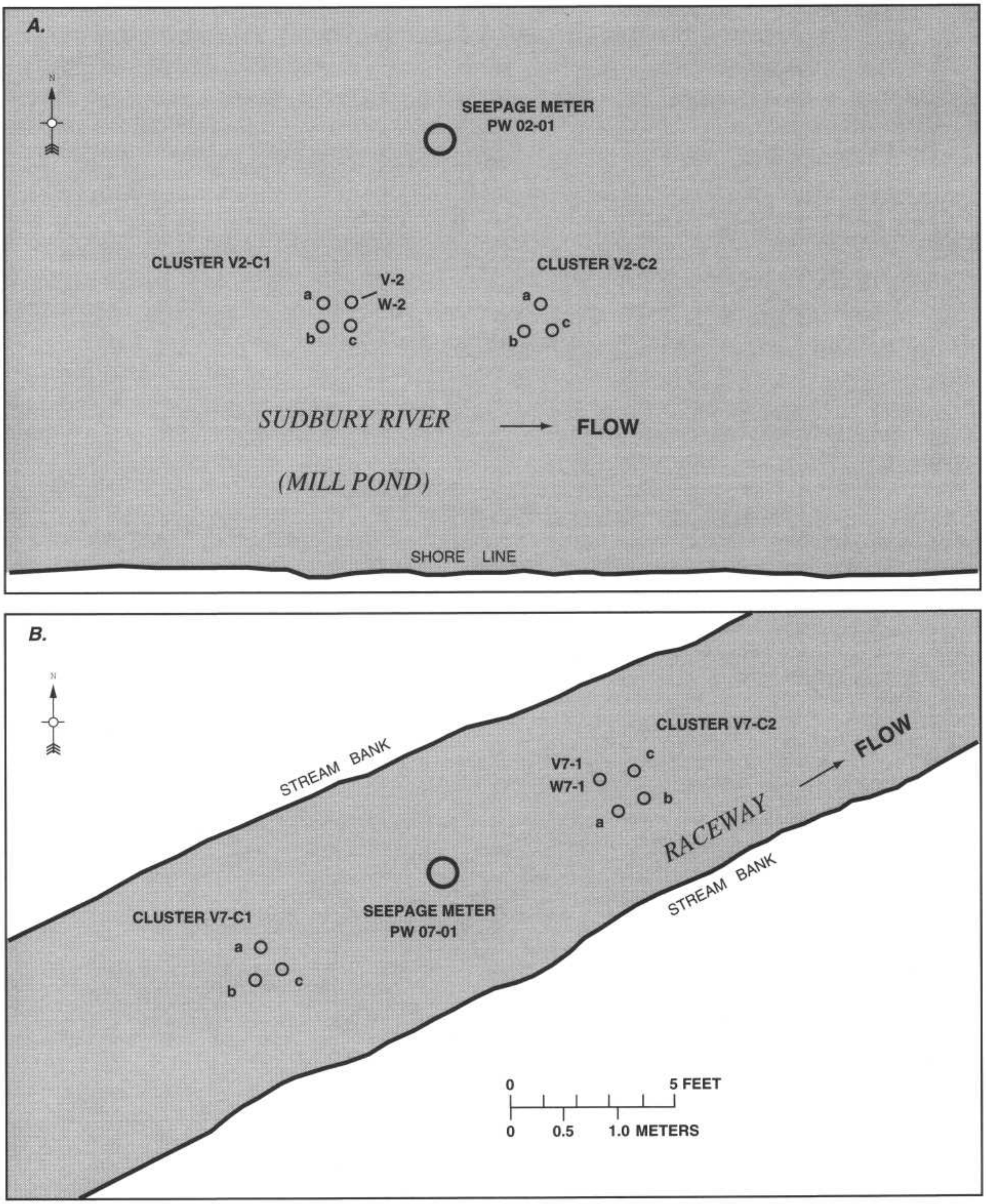


Figure 4. Locations of clusters of vapor-diffusion samplers relative to locations of (*A*) seepage meter PW02-01 and (*B*) seepage meter PW07-01, Ashland, Massachusetts.

Table 2. Concentrations of volatile organic compounds detected in vapor from vapor-diffusion samplers retrieved on February 16, 1999, near the Nyanza Chemical Waste Dump Superfund Site, Ashland, Massachusetts

[**Volatile organic compound:** Compound not detected at the reporting limit given in parentheses. PCE, tetrachloroethene; TCE, trichloroethene; trace, compound detected at concentration below reporting limit. **Other compounds detected and comments:** DCE, dichloroethene; EUPs, early unidentified peaks on gas chromatograph. dup, field duplicate sample; ppb v, parts per billion by volume; --, not analyzed]

Vapor sampler name	Date installed	Bottom material	Volatile organic compound					Other compounds detected and comments
			Benzene (ppb v)	TCE (ppb v)	Toluene (ppb v)	PCE (ppb v)	Chlorobenzene (ppb v)	
Sudbury River in Millpond								
V1	1-19-99	Cobbles and pebbles	(12)	18	(40)	(20)	(40)	EUPs
V1z	1-19-99	Cobbles and pebbles	(12)	23	(40)	(20)	(40)	EUPs. Sampler placed 6 ft from V1
V1a	1-19-99	Organic	(12)	37	(40)	(20)	(40)	Installed in ice-free water near bank
V1a (dup)	1-19-99	Organic	(12)	49	(40)	(20)	(40)	
V1b	1-19-99	Organic	(12)	220	(40)	(20)	52	Installed in ice-free water near bank. EUPs, cis-DCE
V2	1-19-99	Organic -very soft	(12)	560	(40)	(20)	960	At location of V2-C1 cluster.
V2a	1-19-99	Organic	(12)	43	(40)	(20)	520	EUPs, cis-DCE
V2a (dup)	1-19-99	Organic	(12)	80	(40)	(20)	490	EUPs, cis-DCE
V2b	1-19-99	Organic	(12)	340	(40)	(20)	210	EUPs, cis-DCE
V3	1-19-99	Organic	(12)	1,910	(40)	(20)	2,250	EUPs, cis-DCE
V3a	1-19-99	Organic	(12)	23	(40)	(20)	1,270	EUPs, cis-DCE
V3b	1-19-99	Organic	(12)	(12)	(40)	(20)	(40)	EUPs, cis-DCE
V4	1-19-99	Organic	54	430	(40)	(20)	5,330	EUPs, cis-DCE
V4b	1-19-99	Gravel	(12)	(12)	trace	(20)	(40)	EUPs, cis-DCE
V5	1-19-99	Gravel	(12)	(12)	(40)	(20)	(40)	EUPs
Sudbury River Downstream from Dam								
V6	1-19-99	Gravel	(12)	(12)	(40)	(20)	(40)	EUPs
V7-2	1-19-99	Gravel	(12)	(12)	(40)	(20)	78	EUPs
V7a-2	1-19-99	Gravel	(12)	(12)	(40)	(20)	(40)	EUPs
V7a-2 (dup)	1-19-99	Gravel	(12)	(12)	(40)	(20)	(40)	EUPs
V8-2	1-19-99	Gravel	(12)	(12)	(40)	(20)	(40)	EUPs
Former Mill Raceway								
V7-1	1-19-99	Organic	18	590	(40)	(20)	940	EUPs, cis-DCE. Placed at location of V7-C2 cluster.
V7a-1	1-19-99	Organic	55	35	(40)	(20)	1,780	EUPs, cis-DCE
V7a-1 (dup)	1-19-99	Organic	51	37	(40)	(20)	1,630	EUPs, cis-DCE
V7b-1 (lost)	1-19-99	Organic	--	--	--	--	--	Placed between PW7-1 and PW8-1 in raceway
V8-1	1-19-99	Gravel	15	34	(40)	(20)	130	EUPs, cis-DCE
V8a-1	1-19-99	Gravel	15	26	(40)	(20)	93	EUPs, cis-DCE. Located about 1 ft from V8-1.

Although data are limited, results from vapor samplers indicate that the VOCs in bottom sediments along the Sudbury River were present in low concentrations (chlorobenzene detected at a concentration of 78 μg/L at location V7-2) or absent downstream from the dam at the time of the study. The presence of elevated concentrations in samplers placed along the raceway (table 2, fig. 2), however, is consistent with the mapped extent of the contaminant plume in ground water (fig. 2). VOCs detected at location 08-01 in the raceway beyond the mapped extent of the plume may reflect the presence of VOCs in surface water at this location (Roy F. Weston, Inc., 1999b) and an exchange of VOCs between surface water and ground water. Similar conditions for the Royal River near Gray, Maine, downstream from a TCE plume in ground water, have been described by Lyford and others (1999).

EQUILIBRATION TIME FOR VOCS IN DIFFUSION SAMPLERS

Results of analyses for vapor samplers retrieved about once a week from the 4 clusters were not conclusive with regard to equilibration time (table 3, figs. 5*A* and 5*B*). Results of experiments elsewhere have shown that concentrations of VOCs in vapor-diffusion samplers equilibrate within less that 24 hours when placed in a solution that has a known concentration of VOCs. Equilibration after emplacement can be within a period of 24 hours when placed in sandy materials, but can take several days when placed in fine-grained materials (D.A. Vroblesky, U.S. Geological Survey, written commun., 1999). Apparent general increases in concentrations of chlorobenzene and TCE with time at clusters V2-C1 and V7-C2 (table 3, fig. 5) may reflect slow equilibration times of 3 weeks or more at these

Table 3. Concentrations of volatile organic compounds detected in clusters of vapor-diffusion samplers retrieved during January and February 1999 near the Nyanza Chemical Waste Dump Superfund Site, Ashland, Massachusetts

[**Volatile organic compound:** Compound not detected at the reporting limit given in parentheses. PCE, tetrachloroethene; TCE, trichloroethene; trace, compound detected at concentration below reporting limit. **Other compounds detected and comments:** DCE, dichloroethene; EUPs, early unidentified peaks on gas chromatograph. ppb v, parts per billion by volume]

Vapor sampler name	Date installed	Date retrieved	Bottom material	Volatile organic compound					Other compounds detected and comments
				Benzene (ppb v)	TCE (ppb v)	Toluene (ppb v)	PCE (ppb v)	Chloro-benzene (ppb v)	
V2-C1a	1-20-99	1-28-99	Organic	(20)	380	(50)	(30)	650	EUPs, cis-DCE
V2-C1b	1-19-99	2- 2-99	Organic	(12)	610	(40)	(20)	520	EUPs, cis-DCE
V2-C1c	1-19-99	2- 8-99	Organic	(12)	990	(40)	(20)	940	EUPs, cis-DCE; other unidentified peaks
V2	1-19-99	2-16-99	Organic - very soft	(12)	560	(40)	(20)	960	At location of V2-C1 cluster.
V2-C2a	1-19-99	1-28-99	Organic	(12)	330	(50)	(30	160	EUPs, cis-DCE
V2-C2b	1-19-99	2- 2-99	Organic	(12)	770	(50)	(30)	780	EUPs, cis-DCE
V2-C2c	1-19-99	2- 8-99	Organic	(12)	690	(40)	(20)	520	EUPs, cis-DCE; other unidentified peaks
V7-C1a	1-19-99	1-28-99	Organic	(20)	490	(50)	(30)	720	EUPs, cis-DCE
V7-C1b	1-19-99	2- 2-99	Organic	12	73	(40)	(20)	610	EUPs, cis-DCE
V7-C1c	1-19-99	2- 8-99	Organic	trace	170	(40)	(20)	500	EUPs, cis-DCE
V7-C2a	1-20-99	1-28-99	Organic	(20)	150	(50	(30)	52	EUPs, cis-DCE
V7-C2b	1-19-99	2- 2-99	Organic	(12)	390	(40)	(20)	460	EUPs, cis-DCE
V7-C2c	1-19-99	2- 8-99	Organic	(12)	1,330	(40)	40	920	EUPs, cis-DCE
V7-1	1-19-99	2-16-99	Organic	18	590	(40)	(20)	940	EUPs, cis-DCE. Placed at location of V7-C2 cluster.

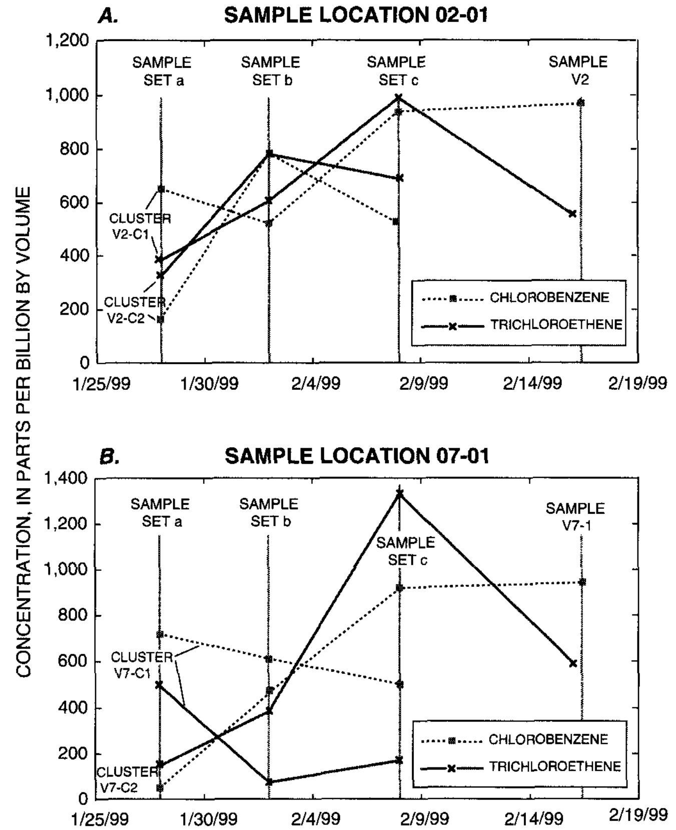


Figure 5. Concentrations of chlorobenzene and trichloroethene detected in vapor-diffusion samplers at (*A*) sample location 02-01 and (*B*) sample location 07-01, January and February 1999, Ashland, Massachusetts.

locations. Other factors, however, that may cause apparent changes in concentrations with time include varying river stages (fig. 3) that affect rates of ground-water flow to or from the stream, spatial variations over short distances, or a combination of these factors. Variability can also be attributed, in part, to the sampling and analytical methods as indicated by differences observed between duplicate samples at sampler V2a (table 2) where chlorobenzene concentrations were similar in the two samples but TCE concentrations differed by a factor of 2. Differing characteristics of bottom sediments (table 2) had no obvious effects on equilibration time. No VOCs were detected in trip blanks transported to the laboratory with cluster samples.

The vapor- and water-diffusion pairs at the locations of clusters V2-C1 and V7-C2 (fig. 4) that were retrieved on February 16, 1999, one week after retrieving the last sample in each cluster of 3 vapor samples at the same locations, provide a fourth sample for comparison to samples collected previously. The concentration of chlorobenzene in the vapor sampler of each pair was about the same as the concentration in the last sampler retrieved, but the concentration of TCE decreased by about one half (table 3). The presence of the water-diffusion sampler may have affected concentrations of VOCs in the vapor-diffusion samplers for unknown reasons. Of possible significance was the observation that several vapor-diffusion samplers were iron-stained upon retrieval, indicating that oxygen was diffusing from air in the bottles to water outside the bottles and altering the geochemistry of the solution locally. It is not known, however, if this process affected concentrations of VOCs in air relative to their concentrations in water.

The possibility that pore water chemistry, including concentration of VOCs, was changing at cluster locations during the study period is supported by specific-conductance measurements for water from seepage meters on January 18 and again on February 15–16, 1999. For example, the specific conductance increased from 360 to 450 μS/cm at seepage meter PW02-01 and from 910 to 1,020 μS/cm at seepage meter PW07-01 between measurements. By contrast, the specific conductance of water in the Sudbury River decreased from about 320 to 250 μS/cm between measurements (Roy F. Weston, Inc., 1999b, Appendix B).

COMPARISON OF CHEMICAL ANALYTICAL RESULTS

VOCs were detected in bottom sediments along the Sudbury River and mill raceway using vapor diffusion-samplers discussed above, water-diffusion samplers, seepage meters, and chemical analyses of the sediments. Each sampling method has its attributes in terms of ease, expense, and reliability of results. This section will qualitatively compare results from the four methods using tables and graphs. Concentrations of VOCs for samples collected by the four methods at each location are given in table 4.

Vapor- and Water-Diffusion Samples

When in equilibrium, the concentration of VOCs in air should correlate with the concentrations in water, as predicted by Henry's Law. Factors that will affect the relation between concentrations in air and concen-

Table 4. Concentrations of volatile organic compounds in vapor-diffusion samplers, water-diffusion samplers, seepage meters, and sediments, December 1998 to February 1999, Nyanza Chemical Waste Dump Superfund Site, Ashland, Massachusetts

[Data for seepage meters and sediment from R.F. Weston, Inc., 1999. **Sample type and units:** PW, seepage meter sample; SD, sediment sample; V, vapor-diffusion sample; W, water-diffusion sample. V and W samples collected on February 16, 1999; PW samples collected on February 15–16, 1999; SD samples collected on December 26–30, 1998. Compound not detected at the reporting limit given in parentheses. J, the compound was detected but near the practical quantitation limit; ns, not sampled or not analyzed; ppb v, parts per billion by volume; µg/kg, micrograms per kilogram; µg/L, micrograms per liter]

Volatile organic compound	Sample type and units	Sample location (fig. 1)									
		01–01	02–01	03–01	04–01	05–01	06–01	07–01	07–02	08–01	08–02
Acetone	V (ppb v)	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	W (µg/L)	4J	(5)	5	4J	6	5J	4J	3J	6	ns
	PW (µg/L)	4J	(5)	3J	3J	(5)	(5)	(5)	(5)	(5)	(5.0)
	SD (µg/kg)	910J	1,000	220J	210J	520	260	340	(240)	(220)	(700)
Benzene	V (ppb v)	(10)	(10)	(10)	54	(10)	(10)	18	(10)	15	(10)
	W (µg/L)	(1.0)	.8J	1	4	(1.0)	(1.0)	1	(1.0)	.8J	ns
	PW (µg/L)	(1.0)	.6J	.8J	3	(1.0)	(1.0)	2	(1.0)	(1.0)	(1.0)
	SD (µg/kg)	(1,600)	(1,000)	(310)	(300)	(410)	(240)	(340)	(240)	(220)	(700)
2-Butanone	V (ppb v)	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	W (µg/L)	4J	(5)	5	(5)	(5)	(5)	(5)	(5)	(5)	ns
	PW (µg/L)	(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)
	SD (µg/kg)	(1,600)	(1,000)	260J	200J	(410)	(240)	480	(240)	(220)	(700)
Chlorobenzene	V (ppb v)	(40)	960	2,250	5,330	(40)	(40)	940	78	130	(40)
	W (µg/L)	(1.0)	50	120	180	(1.0)	(1.0)	61	.8J	5	ns
	PW (µg/L)	(1.0)	38	74	140	(1.0)	.9J	58	(1.0)	2	(1.0)
	SD (µg/kg)	(310)	1,300	120	360	(82)	(49)	980	(49)	(45)	140)
Chloroform	V (ppb v)	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	W (µg/L)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	ns
	PW (µg/L)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	.6J	(1.0)	(1.0)	(1.0)	(1.0)
	SD (µg/kg)	(310)	(210)	(62)	(61)	(82)	(49)	(69)	(49)	(45)	(140)
Chloromethane	V (ppb v)	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	W (µg/L)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	ns
	PW (µg/L)	(2)	(2)	4	(2)	(2)	9	(2)	(2)	(2)	4
	SD (µg/kg)	(620)	(420)	(120)	(120)	(160)	(98)	(140)	(98)	(90)	(280)
1,1-Dichloroethene	V (ppb v)	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	W (µg/L)	(1.0)	(1.0)	1	1	(1.0)	(1.0)	2	(1.0)	(1.0)	ns
	PW (µg/L)	(1.0)	.6J	.5J	1	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)
	SD (µg/kg)	(310)	(210)	(62)	(61)	(82)	(49)	(69)	(49)	(45)	(140)

Table 4. Concentrations of VOCs in vapor-diffusion samplers, water-diffusion samplers, seepage meters, and sediments, December 1998 to February 1999, Nyanza Chemical Waste Dump Superfund site, Ashland, Massachusetts—*Continued*

Volatile organic compound	Sample type and units	Sample location (fig. 1)									
		01–01	02–01	03–01	04–01	05–01	06–01	07–01	07–02	08–01	08–02
cis-1,2-Dichloroethene (cis-DCE) (total 1,2-Dichloroethene for sediment samples)	V (ppb v)	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	W (µg/L)	(2.0)	25	70	70	(2.0)	(2.0)	62	(2.0)	4	ns
	PW (µg/L)	(2.0)	47	44	60	(2.0)	(2.0)	67	(2.0)	5	(2.0)
	SD (µg/kg)	(310)	230	(72)	44J	(82)	(49)	240	(49)	(45)	(140)
trans-1,2-Dichloroethene	V (ppb v)	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	W (µg/L)	(2.0)	(2.0)	1J	(2.0)	(2.0)	(2.0)	1J	(2.0)	(2.0)	ns
	PW (µg/L)	(2.0)	(2.0)	(2.0)	(2.0)	(2.0)	(2.0)	1J	(2.0)	(2.0)	(2.0)
	SD (µg/kg)	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Ethylbenzene	V (ppb v)	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	W (µg/L)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	4	(1.0)	ns
	PW (µg/L)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	--	(1.0)
	SD (µg/kg)	(1,600)	(1,000)	(310)	(300)	(410)	(240)	(340)	(240)	(220)	(700)
Tetrachloroethene (PCE)	V (ppb v)	(20)	(20)	(20)	(20)	(20)	(20)	(20)	(20)	(20)	(20)
	W (µg/L)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	.5J	(1.0)	(1.0)	ns
	PW (µg/L)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)
	SD (µg/kg)	(310)	(1,000)	(62)	(61)	(82)	(49)	(69)	(49)	(45)	(140)
Toluene	V (ppb v)	(40)	(40)	(40)	(40)	(40)	(40)	(40)	(40)	(40)	(40)
	W (µg/L)	(1.0)	(1.0)	.7J	.8J	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	ns
	PW (µg/L)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)
	SD (µg/kg)	(1,600)	(1,000)	(310)	(300)	(410)	(240)	(340)	(240)	(220)	(700)
Trichloroethene (TCE)	V (ppb v)	18	560	1,910	430	(12)	(12)	590	(12)	34	(12)
	W (µg/L)	1	5	110	11	(1.0)	(1.0)	22	(1.0)	4	ns
	PW (µg/L)	1	16	60	16	(1.0)	(1.0)	35	(1.0)	5	(1.0)
	SD (µg/kg)	(310)	240	(62)	(61)	(82)	(49)	700	(49)	(45)	(140)
Vinyl chloride	V (ppb v)	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	W (µg/L)	(2.0)	13	9	67	(2.0)	(2.0)	19	(2.0)	2	ns
	PW (µg/L)	(2.0)	6	7	58	(2.0)	(2.0)	23	(2.0)	3	(2.0)
	SD (µg/kg)	(620)	(420)	(120)	(120)	(160)	(98)	(140)	(98)	(90)	(280)
Total Xylenes	V (ppb v)	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	W (µg/L)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	29	(1.0)	ns
	PW (µg/L)	(1.0)	0.7J	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)
	SD (µg/kg)	(1,600)	(1,000)	(310)	(300)	(410)	(240)	(340)	(240)	(220)	(700)

trations in water are temperature, pressure, and molecular weight of a compound. Calculations made using information provided by Rathbun (1998) about Henry's Law constants and their variation with temperature indicate that TCE concentrations in air, in units of parts per billion by volume, can be 20 to 30 times its concentration in water, in micrograms per liter, for a temperature range of 1°C to 10°C. For chlorobenzene, the concentration in air can be from 10 to 16 times its concentration in water for that same temperature range.

Several VOCs were detected in water from water-diffusion samplers, but the principal compounds and maximum concentrations detected were for chlorobenzene (180 µg/L at location 04-01), TCE (110 µg/L at location 03-01), cis-DCE (70 µg/L at locations 03-01 and 04-01), and vinyl chloride (67 µg/L at location 04-01) (table 4). Chemical analyses for water included a larger number of chemicals than the 5 target compounds for vapor-diffusion samples. Table 4 reports all of the VOCs that were detected in the water-diffusion samples. In general, the target compounds detected in vapor samples were consistent with compounds detected in water samples at each sampling location. Exceptions were benzene, which was detected in vapor samples at only three of the five locations where it was detected in water samples, and toluene, which was detected at low concentrations (less than 1 µg/L) at two locations (03-01 and 04-01) in water samples but not in vapor samples at the same locations.

Figure 6 shows the relation of concentrations in vapor to concentrations in water at vapor- and water-diffusion sampler pairs for chlorobenzene and TCE, the major compounds detected in vapor and water. Also shown is the range of concentrations that might be expected on the basis of Henry's Law, assuming a temperature range of 1°C to 10°C and samples collected at atmospheric pressure. The temperature range from 1°C to 10°C represents a possible range during the study period from near 0°C at times in surface water to a maximum of 10°C in ground water. Although a fair correlation is apparent for the two types of samples, deviations from concentrations predicted by Henry's Law indicate that either the vapor samples, water samples, or both, had not equilibrated with sediment pore water. Uncertainties in chemical analytical results could also affect the apparent relation between concentrations in air and concentrations in water.

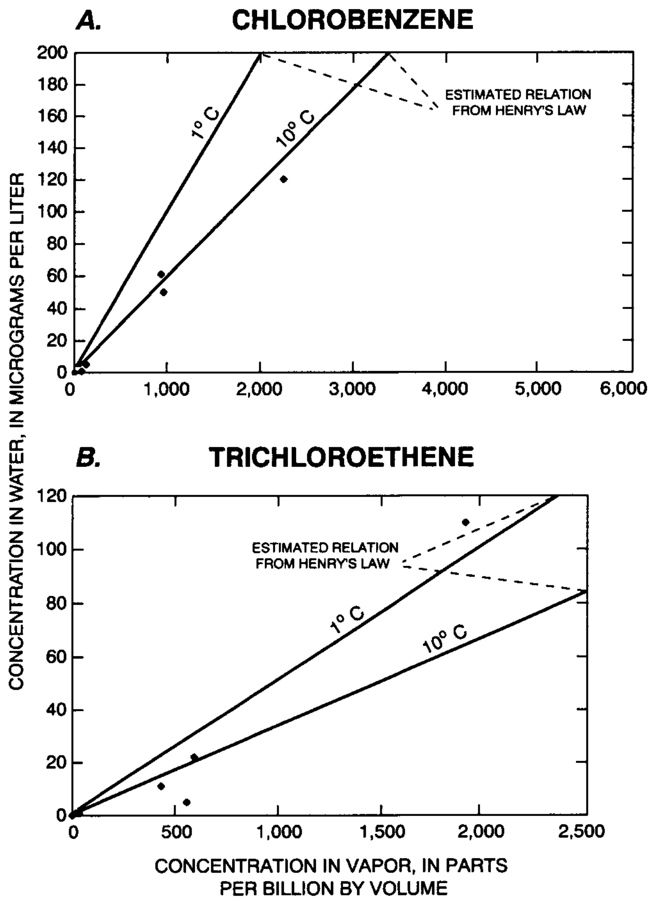


Figure 6. Concentrations of (*A*) chlorobenzene and (*B*) trichloroethene in vapor- and water-diffusion samplers, February 16, 1999, Ashland, Massachusetts.

Water-Diffusion Samples and Seepage-Meter Samples

Results of chemical analyses of water samples extracted from seepage meters (Roy F. Weston, Inc., 1999b) are included in table 4 for comparison to results from water-diffusion samplers. In general, the principal compounds detected by the two methods are consistent, and concentrations for the major constituents are similar, as shown in figure 7. At concentrations of individual constituents greater than about 50 µg/L, the concentrations in water-diffusion samples were generally higher than concentrations in seepage-meter samples. This indicates that analyses of water from seepage meters may have underestimated concentrations in pore water. If the water-diffusion samplers had not fully equilibrated, as discussed above, then both methods may underestimate actual concentrations in pore water, at least at the higher concentrations.

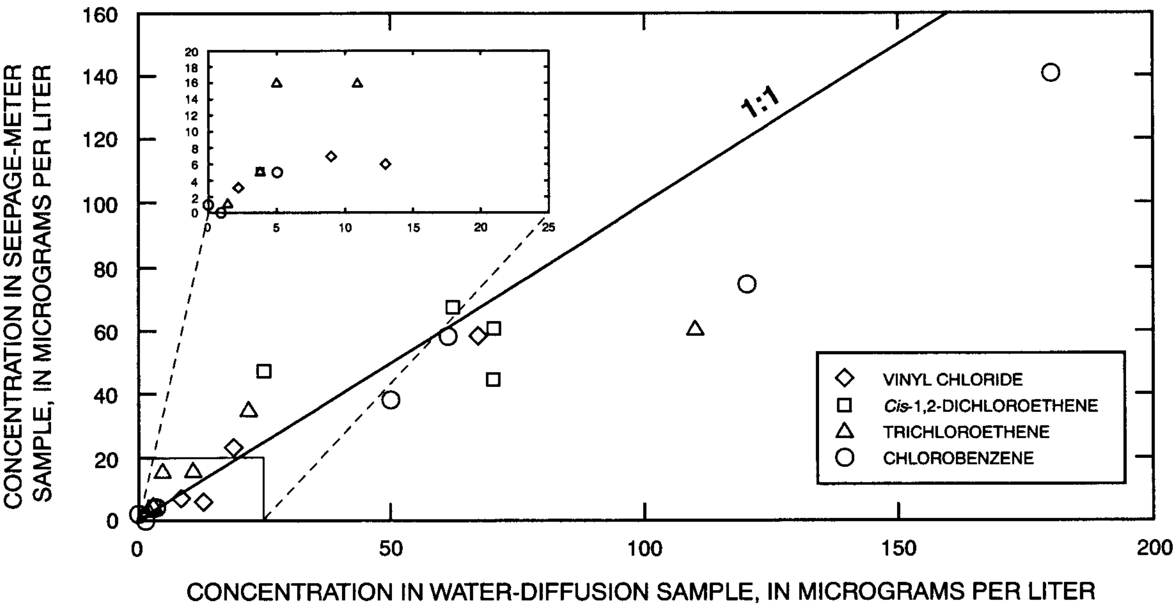


Figure 7. Concentrations of selected volatile organic compounds detected in water-diffusion samplers and concentrations in water from seepage meters, Ashland, Massachusetts.

Several compounds that were present near the detection limit in some diffusion samplers were not detected in nearby seepage meters, and some compounds were detected in seepage meters but not in diffusion samplers. Compounds that were present in concentrations appreciably above the detection limit were total xylenes, which were detected in diffusion sampler W7-2 but not in the nearby seepage meter, and chloromethane, detected in water from seepage meters PW03-01 and PW06-01 but not in nearby diffusion samplers. No patterns that might be related to the sampling method were apparent. Differences in compounds detected and concentrations may be attributable, in part, to variations in plume chemistry over distances of several feet between the seepage meters and diffusion samplers.

Water-Diffusion Samples and Sediment Samples

Results of chemical analyses of sediment samples collected at the locations of seepage meters (Roy F. Weston, Inc., 1999b) are included in table 4 for comparison to results from other sampling methods. In general, the principal VOCs detected in sediment are consistent with those detected in water-diffusion samplers (and water from seepage meters as discussed above). Examination of concentrations reported in table 4 [accounting for different units for the two types of samples (µg/L for water and µg/kg for sediment)], however, indicate a poor correlation for the two methods. At several locations, such as 01-01, 03-01, 04-01, and 08-01, TCE was present in water-diffusion samples but was not detected in sediment samples. Other compounds that were detected in water-diffusion samples but not in sediment included vinyl chloride, 1,1,-dichloroethene, and benzene. The apparent absence of some compounds in sediments may result from relatively high quantitation limits for the sediment analyses and a shallower sampling depth (6 in. or less) than the depths of the water-diffusion samplers (6 to 8 in.). These results indicate that the other three sampling methods yielded a better representation of the VOCs present in sediments than chemical analyses of the sediments. Concentrations of total organic carbon at the sampling locations considered here ranged from 4,900 to 116,000 mg/kg (Roy F. Weston, Inc., 1999b). The relative concentration of VOCs in water samples and sediment samples are not obviously affected by the concentration of total organic carbon in sediment, although this possibility cannot be thoroughly assessed with the limited data available.

USE OF DIFFUSION SAMPLERS AS RECONNAISSANCE TOOLS

This study has reaffirmed that vapor-diffusion samplers placed in bottom sediments are useful reconnaissance tools for determining the distribution of VOCs in ground water and variations in concentrations across the width of a contaminant plume that discharges to a surface-water body. Others who have demonstrated uses of vapor-diffusion samplers for this purpose include Vroblesky and others (1996), Savoie and others (1999), and Lyford and others (1999). Sampling results can also provide useful information about ground-water flow patterns. For example, the vapor samplers used for this study, although few in number, confirmed a likely losing reach in the downstream end of the mill pond and indicated minimal discharge of contaminants to the Sudbury River downstream from the dam. This scenario differs from a previous conceptual model of contaminant movement that showed the plume of contaminants extending to the Sudbury River (fig. 2). Although beyond the scope of this study, a network of vapor-diffusion samplers placed within the mill pond area might have identified discharge points for ground water that contained higher concentrations of VOCs, consistent with concentrations in deep ground water, than those apparent near the shore. Networks of vapor-diffusion samplers have been used to delineate ground-water discharge areas and flow patterns near ponds on Cape Cod (D.R. LeBlanc, U.S. Geological Survey, oral commun., 1999). Diffusion samplers may have limitations where VOCs are present in surface water, because the source of VOCs could be either surface water or ground water.

Experience at the Nyanza site and other sites in New England has demonstrated that one person can construct as many as 100 samplers per day, and a crew of 3 can install 50 to 150 samplers per day; these totals depend somewhat on ease of access to the study area and character of the bottom sediments. Retrieval times and personnel requirements are less for retrieval than for installation. An analyst using a gas chromatograph can analyze about 50 vapor samples in a day. Therefore, a considerable amount of information can be generated in a short time relative to other sampling methods.

Comparison of VOCs in vapor-diffusion samplers to VOCs in adjacent water-diffusion samplers indicates that different equilibration times after emplacement might limit the use of either method for reliably determining actual concentrations of VOCs in pore water. At present, the equilibration times for various types of bottom materials and various hydrologic conditions are not well defined. Other factors that might affect concentrations and interpretation of results are time-varying hydrologic conditions that affect the flux of contaminated ground water to streams, variations in concentrations over short distances, and exchanges between ground water and surface water in the hyporheic zone, which is the subsurface zone where stream water flows through short segments of its adjacent beds and banks (Winter and others, 1998).

The results of this study indicates that water-diffusion samplers are a viable alternative to seepage meters for identifying the types of VOCS that are present in bottom sediments. A water-diffusion sampler can be constructed, installed, and retrieved in a total time of an hour or less. This contrasts with a time of several hours for installation and sampling of seepage meters. Seepage meters or other techniques for sampling pore water, however, are needed to determine concentrations of other contaminants such as metals or SVOCs in bottom sediments.

Elevated concentrations of SVOCs and metals in ground water near the Nyanza site are associated with elevated concentrations of VOCs (Roy F. Weston, Inc., 1998). This condition is commonly observed at contaminated sites. In areas where VOCs are indicators of other contaminants in ground water, vapor-diffusion samplers can quickly and economically identify "hot spots" and guide the sampling of bottom sediments for other contaminants.

Vapor- and water-diffusion samplers may be useful for assessing geochemical processes such as biodegradation in bottom sediments. For example, results from water-diffusion samplers and seepage meters identified elevated concentrations of vinyl chloride (9 to 67 µg/L in water-diffusion samples) at four locations. Concentrations of vinyl chloride in water from wells near the river and raceway where ground water is discharging to surface water, however, are generally less than 2 µg/L. This concentration pattern indicates possible transformation of TCE by biodegradation as ground water moves upward through the organic-rich bottom sediments toward surface water. Biodegradation of chlorinated VOCs as ground water flows vertically upward through wetland sediment has been described by Lorah and Olsen (1999). A network of vapor- or water-diffusion samplers could be useful for identifying active areas of biodegradation for chlorinated VOCs. Networks of vapor-diffusion samplers may also be useful for studying patterns of exchanges between surface water and ground water in the hyporheic zone, where VOCs are known to be discharging from ground water to surface water.

Because results from this study and studies in other New England settings have confirmed the value of vapor-diffusion samplers as simple and economical reconnaissance tools, further testing for this purpose is not warranted. If a goal is to determine actual concentrations of VOCs at the interface between ground water and surface water, however, additional studies are needed to evaluate equilibration times in various geohydrologic settings. Also needed to accomplish this goal is a better understanding of variations in concentrations over short distances of a few feet and possible changes in concentrations with changing hydrologic conditions. Networks of closely-spaced vapor samplers retrieved and analyzed over an extended time in several geohydrologic settings could provide useful insights on spatial and temporal variability.

SUMMARY

Polyethylene-membrane water-to-vapor (vapor) and water-to-water (water) diffusion samplers were installed during a pilot study in January 1999 in bottom sediments along the Sudbury River and former mill raceway to determine if vapor samplers would be useful in this setting for delineating a plume of contaminants in ground water near the river and raceway, to evaluate equilibration time for vapor-diffusion samplers, and to determine if diffusion samplers might be an alternative to seepage meters (inverted steel drums) and sediment sampling for evaluating concentrations of VOCs in bottom sediments.

VOCs were detected in all but 5 of 21 vapor-diffusion samplers (excluding samples from clusters and duplicate samples). Of 5 tested compounds—benzene, trichloroethene, toluene, tetrachloroethene, and chlorobenzene—chlorobenzene and trichloroethene were detected most frequently. The distribution of VOCs was generally consistent with the mapped plume of contaminants in ground water. The absence of VOCs in the downstream part of the mill pond was consistent with water-level well data, which indicated that water was leaking from the pond to the surficial aquifer in this area. The general absence of VOCs along the Sudbury River downstream from the dam indicated that the discharge of VOCs to the river was limited at the time of the study. Result from the experiment to evaluate equilibration times for vapor-diffusion samplers were inconclusive because of changing hydrologic conditions that may have affected concentrations of VOCs, possible variations in concentrations of VOCs over short distances, and imprecise sampling and analytical methods. The limited data from this study, however, indicated that equilibration times may exceed 3 weeks in some settings.

Analyses of water from water-diffusion samplers included a larger suite of chemicals than analyses for vapor from vapor-diffusion samplers. The principal compounds and maximum concentrations detected in water-diffusion samplers were chlorobenzene (180 μg/L), trichloroethene (110 μg/L), cis 1,2-dichloroethene (70 μg/L), and vinyl chloride (67 μg/L). Highest concentrations of TCE and chlorobenzene in water samples were found at the same locations as the highest concentrations detected in vapor samples. Concentrations of chlorobenzene and TCE detected in vapor-diffusion samplers generally correlated with concentrations detected in water-diffusion samplers. Also, the VOCs and concentrations detected in water-diffusion samplers were generally consistent with those detected in water from seepage meters.

Results from this pilot study reaffirm results from previous studies that diffusion samplers are a simple and economical means of identifying "hot spots" for contaminants in bottom sediments, and can provide insights on pathways for contaminants near surface-water bodies. Diffusion samplers may also be useful for studying variations in concentrations of VOCs across short distances, variations with time and changing hydrologic conditions, and processes such as chemical transformations and exchanges between surface water and ground water in the hyporheic zone.

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