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Guidance on the Use of Passive-Vapor-Diffusion Samplers to Detect Volatile Organic Compounds in Ground-Water-Discharge Areas, and Example Applications in New England

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CONTENTS

Abstract 1
Introduction 1
Advantages and Limitations of Passive-Vapor-Diffusion Samplers 3
Advantages 3
Limitations 4
PART 1. Guidance on the Use of Passive-Vapor-Diffusion Samplers 5
By Don A. Vroblesky
Assembly of Samplers 5
Deployment of Samplers 9
Recovery of Samplers 13
Factors Affecting Deployment of Samplers and Data Interpretation 16
Quality Control and Assurance 17
PART 2. Example Applications in New England 18
Eastern Surplus Company Superfund Site, Meddybemps, Maine 20
By Forest P. Lyford and Edward M. Hathaway
Description of Study Area 20
Purpose and Design of Sampling 23
Results 23
McKin Company Superfund Site, Gray, Maine 25
By Forest P. Lyford, Terrence R. Connelly, and Laura E. Flight
Description of Study Area 25
Purpose and Design of Sampling 25
Results 28
Nutmeg Valley Road Superfund Site, Wolcott and Waterbury, Connecticut 28
By John R. Mullaney, Peter E. Church, and Carolyn J. Pina-Springer
Description of Study Area 28
Purpose and Design of Sampling 31
Results 31
Baird & McGuire Superfund Site, Holbrook, Massachusetts 34
By Jennifer G. Savoie and Melissa G. Taylor
Description of Study Area 34
Purpose and Design of Sampling 34
Results 34
Allen Harbor Landfill, Davisville Naval Construction Battalion Center Superfund Site, North Kingstown, Rhode Island 37
By Forest P. Lyford, William C. Brandon, and Christine A. P. Williams
Description of Study Area 37
Purpose and Design of Sampling 37
Results 40
Calf Pasture Point, Davisville Naval Construction Battalion Center Superfund Site, North Kingstown, Rhode Island 40
By Forest P. Lyford, Christine A. P. Williams, and William C. Brandon
Description of Study Area 40
Purpose and Design of Sampling 43
Results 43
Otis Air National Guard/Camp Edwards Superfund Site, Johns Pond, Falmouth, Massachusetts 43
By Jennifer G. Savoie and Denis R. LeBlanc
Description of Study Area 43

Purpose and Design of Sampling 45
Results 45
Nyanza Chemical Waste Dump Superfund Site, Ashland, Massachusetts 48
By Forest P. Lyford, Richard E. Willey, and Sharon M. Hayes
Description of Study Area 48
Purpose and Design of Sampling 51
Results 51
Centredale Manor Restoration Project Superfund Site, North Providence, Rhode Island 52
By Peter E. Church, Forest P. Lyford, and Anna F. Krasko
Description of Study Area 52
Purpose and Design of Sampling 54
Results 54
Quality-Assurance Procedures 54
Summary and Conclusions 56
References Cited 58
Appendix 1. Laboratory and Field Testing of Passive-Vapor-Diffusion Sampler Equilibration Times, Temperature Effects, and Sample Stability 63
By Don A. Vroblesky
Equilibration Times and Temperature Effects 65
Sample Stability 71
Appendix 2. Field Screening of Volatile Organic Compounds Collected with Passive-Vapor-Diffusion Samplers with a Gas Chromatograph 73
By Scott Clifford

FIGURES

1–9. Photographs showing:
1. Glass vial in two layers of polyethylene tubing 2
2. Passive-vapor-diffusion samplers with (*A*) vial and screw cap, (*B*) uncapped glass vial sealed in polyethylene tubing and secured to wire surveyor flag, and (*C*) glass vial sealed in polyethylene sandwich bags and secured to wire surveyor flag 6
3. Heat sealing of glass vial in polyethylene tubing 7
4. Glass vial positioned in sandwich bag so that a single layer of low-density polyethylene is tight across the opening and the self-locking nylon tie does not interfere with capping 8
5. Installation method for passive-vapor-diffusion samplers in water 0 to 2 feet deep 10
6. Drive-point assembly for installation of passive-vapor-diffusion sampler in water 2 to 4 feet deep in clayey silt to coarse sand and gravel sediments 11
7. Drive-point method for installation of passive-vapor-diffusion sampler in water 2 to 4 feet deep in clayey silt to coarse sand and gravel sediments 12
8. Screwing a septated cap onto a glass vial encased in the inner low-density polyethylene tubing 14
9. (*A*) Attaching and (*B*) crimping a septated cap onto a glass vial encased in the inner low-density polyethylene tubing 15

10–21 Maps showing:
10. Locations of sites in New England where passive-vapor-diffusion samplers have been used to detect and delineate discharge areas of ground water contaminated by volatile organic compounds into surface-water bodies 19
11. Location of the Eastern Surplus Superfund Site and study area, Meddybemps, Maine 21
12. Potentiometric surfaces and generalized ground-water-flow directions for the surficial and bedrock aquifers, Eastern Surplus Superfund Site, Meddybemps, Maine, April 30, 1997 22
13. Concentrations of tetrachloroethene (PCE) in passive-vapor-diffusion samplers installed in river-bottom sediments on the western edge of Dennys River, Meddybemps, Maine, October 1996 24
14. Location of the McKin Superfund Site and study area, potentiometric surface contours for the surficial aquifer, and extent of trichloroethene in ground water, Gray, Maine 26

15. Locations of passive-vapor-diffusion samplers installed in river-bottom sediment along and near the Royal River in September and October 1997, and extent of trichloroethene in ground water, Gray, Maine 27
16. Concentrations of trichloroethene in passive-vapor-diffusion samplers installed in river-bottom sediments near Boiling Springs, Gray, Maine, September and October 1997 29
17. Location of the Nutmeg Valley Road Superfund Site and study area, Nutmeg Valley, Wolcott and Waterbury, Connecticut 30
18. Concentrations of trichloroethene plus tetrachloroethene in passive-vapor-diffusion samplers installed in river-bottom sediments of the Mad River, Old Tannery Brook, and an unnamed stream, Nutmeg Valley, Wolcott and Waterbury, Connecticut, July 1997 32
19. Concentrations of trichloroethene plus tetrachloroethene in passive-vapor-diffusion samplers installed in river-bottom sediments of the Mad River, Old Tannery Brook, and an unnamed stream, Nutmeg Valley, Wolcott and Waterbury, Connecticut, November 1997 33
20. Location of the Baird & McGuire Superfund Site and study area, Holbrook, Massachusetts 35
21. Concentrations of trichloroethene plus tetrachloroethene and petroleum compounds in passive-vapor-diffusion samplers installed in river-bottom sediments of the Cochato River, Baird & McGuire Superfund Site, Holbrook, Massachusetts, March and April 1998 36

22. Aerial photograph showing locations of the Allen Harbor Landfill and Calf Pasture Point study areas, Davisville Naval Construction Battalion Center Superfund Site, North Kingstown, Rhode Island 38

23–33. Maps showing:

23. Directions of ground-water flow in the shallow and deep surficial aquifers, concentrations of volatile organic compounds in ground water beneath the Allen Harbor Landfill, December 1995, and concentration of trichloroethene in passive-vapor-diffusion samplers installed in tidal-zone sediments along the shoreline of Allen Harbor Landfill, April 1998, Davisville Naval Construction Battalion Center Superfund Site, North Kingstown, Rhode Island 39
24. Potentiometric surfaces and generalized ground-water-flow directions for the shallow and deep surficial aquifers, Calf Pasture Point, Davisville Naval Construction Battalion Center Superfund Site, North Kingstown, Rhode Island, December 1995 41
25. Concentrations of trichloroethene in passive-vapor-diffusion samplers installed in the tidal-zone sediments along the shoreline and in wetland-bottom sediments near the shoreline, Calf Pasture Point, Davisville Naval Construction Battalion Center Superfund Site, North Kingstown, Rhode Island, March and April 1998 42
26. Locations of the Johns Pond study area and Storm Drain-5 contaminant plume, and the altitude of water table (March 1993), Cape Cod, Massachusetts 44
27. Concentrations of trichloroethene plus tetrachloroethene in passive-vapor-diffusion samplers installed in pond-bottom sediments adjacent to the Storm Drain-5 contaminant plume, Johns Pond, Cape Cod, Massachusetts, August 1998 46
28. Concentrations of trichloroethene in passive-vapor-diffusion samplers installed in pond-bottom sediments in the zones where high concentrations (greater than 10,000 part per billion by volume) of trichloroethene were detected with passive-vapor-diffusion samplers in August 1998, Johns Pond, Cape Cod, Massachusetts, December 1998 47
29. Discharge areas delineated with passive-vapor-diffusion samplers, August and December 1998, and ground-water pathways of the Storm Drain-5 plume and trichloroethene plumes, Johns Pond, Cape Cod, Massachusetts 48
30. Location of Nyanza Chemical Waste Dump Superfund Site, passive-vapor-diffusion sampler locations, potentiometric-surface contours for the surficial aquifer, and directions of ground-water flow, Ashland, Massachusetts 49
31. The extent of contaminants in ground water and concentrations of chlorobenzene and trichloroethene detected in passive-vapor-diffusion samples, Nyanza Chemical Waste Dump Superfund Site, Ashland, Massachusetts, February 1999 50
32. Locations of the Centredale Manor Restoration Project Superfund Site and study area, North Providence, Rhode Island 52

33. Concentrations of trichloroethene plus tetrachloroethene in passive-vapor-diffusion samplers installed in channel-bottom sediments of the Woonasquatucket River, a former mill raceway, and a cross channel, Centredale Manor Restoration Project Superfund Site, North Providence, Rhode Island, September 1999 53

1A–1D. Graphs showing:

1A. Changes in concentrations of volatile organic compounds in passive-vapor-diffusion samples over time at 21 degrees Celsius under laboratory conditions in a mixed solution of volatile organic compounds with aqueous concentrations less than 100 micrograms per liter 68

1B. Changes in concentrations of volatile organic compounds in passive-vapor-diffusion samples over time at 10 degrees Celsius under laboratory conditions in a mixed solution of volatile organic compounds with aqueous concentrations ranging from 430 to 570 micrograms per liter 69

1C. Ratio over time of (*A*) toluene and (*B*) tetrachloroethene gas concentrations by volume (parts per billion) in passive-vapor-diffusion samplers to aqueous concentrations by mass (210 to 310 micrograms per liter of toluene and 110 to 340 micrograms per liter of tetrachloroethene) in a test solution containing the diffusion samplers in 1.9-liter jars at average temperatures of 22.4, 9.5, and 1.4 degrees Celsius 70

1D. Changes in trichloroethene concentrations over time in passive-vapor-diffusion samples from contaminated ground-water discharge areas in South Carolina in (Site 1) Coastal Plain sediments and (Site 2) Piedmont sediments with differing sediment types and vertical hydraulic gradients 71

TABLES

1. Volatile organic compounds detected under field conditions with passive-vapor-diffusion samplers at contaminated ground-water-discharge areas in New England and South Carolina and the range of minimum reporting limits for these compounds at the nine New England sites 3

2. Superfund sites in New England where passive-vapor-diffusion samplers were used to detect and delineate volatile organic compounds in bottom sediment of surface-water bodies, hydrologic setting, principal compounds detected, and maximum vapor concentration measured 20

3. Number and distribution of duplicate samples from the nine study sites in New England 55

4. Relative percent differences of volatile organic compound (VOC) concentrations in duplicate samples where a VOC was detected above the reporting limit in both samples from the nine study sites in New England 56

1A. Average concentrations and standard deviations of volatile organic compounds in passive-vapor-diffusion samplers over time at 21 degrees Celsius under laboratory conditions in 480-milliliter test jars with spiked concentrations less than100 micrograms per liter 66

1B. Average concentrations and standard deviation of volatile organic compounds in passive-vapor-diffusion samplers over time at 10 degrees Celsius under laboratory conditions in 1.9-liter test jars with spiked concentrations ranging from 430 to 570 micrograms per liter 66

1C. Ratio of concentrations from passive-vapor-diffusion samplers to aqueous-phase concentrations for toluene and tetrachloroethene over time at various temperatures under laboratory conditions in 1.9-liter test jars containing 210 to 310 micrograms per liter of toluene and 110 to 340 micrograms per liter of tetrachloroethene 67

1D. Average concentrations and standard deviations of trichloroethene over time in passive-vapor-diffusion samples in bottom sediment of streams at contaminated ground-water discharge areas in the Coastal Plain (site 1) and the Piedmont (site 2) of South Carolina, 1998 72

2A. Typical achievable reporting limits for volatile organic compounds commonly detected in passive-vapor-diffusion samplers from a gas chromatograph equipped with a photoionization detector and an electron capture detector 76

2B. Vapor concentrations of volatile organic compounds commonly detected with passive-vapor-diffusion samplers in the head space of a 10 micrograms per liter aqueous standard at approximately 0 to 1 degree Celsius 77

2C. Quality controls, acceptance criteria, and corrective actions 79

CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

CONVERSION FACTORS

Multiply	By	To obtain
acre	0.4047	hectare
feet (ft)	0.3048	meters
feet per day (ft/d)	0.3048	meters per day
inches (in.)	2.54	centimeters
mil	0.0254	millimeters
square feet (ft^2)	0.0929	square meters

Temperature in degrees Celsius (°C) can 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 the Sea Level Datum of 1929.

ABBREVIATIONS

µg/L	micrograms per liter
mg/L	milligrams per liter
mL	milliliter
mol/m^3	moles per cubic meter
PCE	tetrachloroethene
ppb v	parts per billion by volume
PVC	polyvinylchloride
PVD sampler	passive-vapor-diffusion sampler
SVOCs	semi-volatile organic compounds
TCE	trichloroethene
VOCs	volatile organic compounds
cis-DCE	*cis*-1,2-dichloroethene

Concentration of chemical constituents in air are given in parts per billion by volume (ppb v).

Concentration of chemical constituents in water are given in micrograms per liter (µg/L).

Guidance on the Use of Passive-Vapor-Diffusion Samplers to Detect Volatile Organic Compounds in Ground-Water-Discharge Areas, and Example Applications in New England

By Peter E. Church, Don A. Vroblesky, Forest P. Lyford, *and* Richard E. Willey

Abstract

Polyethylene-membrane passive-vapor-diffusion samplers, or PVD samplers, have been shown to be an effective and economical reconnaissance tool for detecting and identifying volatile organic compounds (VOCs) in bottom sediments of surface-water bodies in areas of ground-water discharge. The PVD samplers consist of an empty glass vial enclosed in two layers of polyethylene membrane tubing. When samplers are placed in contaminated sediments, the air in the vial equilibrates with VOCs in pore water. Analysis of the vapor indicates the presence or absence of VOCs and the likely magnitude of concentrations in pore water.

Examples of applications at nine hazardous-waste sites in New England demonstrate the utility of PVD samplers in a variety of hydrologic settings, including rivers, streams, ponds, wetlands, and coastal shorelines. Results of PVD sampling at these sites have confirmed the presence and refined the extent of VOC-contaminated ground-water-discharge areas where contaminated ground water is known, and identified areas of VOC-contaminated ground-water discharge where ground-water contamination was previously unknown. The principal VOCs detected were chlorinated and petroleum hydrocarbons. Vapor concentrations in samplers range from not detected to more than 1,000,000 parts per billion by volume. These results provided insights about contaminant distributions and ground-water-flow patterns in discharge areas, and have guided the design of focused characterization activities.

INTRODUCTION

Passive-vapor-diffusion (PVD) samplers are designed and primarily used as a reconnaissance tool to detect and identify volatile organic compound (VOC) contaminated ground water discharging into surface-waters bodies at and near hazardous-waste sites (Vroblesky and others, 1996; Vroblesky and Robertson, 1996; Vroblesky and Hyde, 1997). Determining the location of discharging contaminated ground water is important for plume mapping, evaluating risk potential to human health and the environment, and designing focused site-characterization and monitoring activities. Applications of PVD samplers at and near nine hazardous-waste sites in New England demonstrated the samplers' effectiveness in detecting and delineating VOCs in a variety of hydrologic settings including rivers, streams, ponds, wetlands, and coastal shorelines. The PVD samplers also have been used successfully as passive-soil-gas samplers in unsaturated zones to map ground-water contamination (Vroblesky and others, 1992).

The PVD samplers, developed by the U.S. Geological Survey (USGS) (Vroblesky and others, 1996) consist of an empty, uncapped, glass vial enclosed in two layers of low-density polyethylene membrane tubing (fig. 1) that are permeable to many VOCs of environmental interest, such as petroleum and chlorinated compounds (table 1), but not permeable to water (Vroblesky and others, 1991). When samplers are buried in VOC-contaminated pore water in the bottom sediment of surface-water bodies, an equilibrium begins to develop between VOC concentrations in water and the air in the vial. Equilibrium times, which are dependent on many factors such as hydraulic conductivity of the sediment and temperature of the pore water, generally range from 1 to 3 weeks. During sampler recovery the outer tubing, which is used to prevent sediment, which may be contaminated, from coming into contact with the inner tubing and the opened vial, is removed. A cap is then screwed on to the vial, thereby securing the inner tubing tight against the vial opening to prevent loss of VOCs vapor in equilibrium with water concentrations at the sampler deployment point.

Concentrations of VOCs detected in air in a sampler indicate vapor-phase concentrations in sediment-pore water. The relative concentration partitioning into the air and water varies among VOCs and is described by Henrys' law constant for the particular VOC. A compound with a relatively high vapor pressure and low solubility will tend to become more concentrated in the vapor phase than in the water phase. Several of VOCs with lower vapor pressure tend to be more concentrated in the water phase, but still maintain a vapor-phase signature. Because the low-density polyethlene membrane tubing is not a major barrier to VOC diffusion over time, PVD samplers provide a vapor phase into which VOCs can diffuse from the aqueous phase. The VOCs in water near PVD samplers diffuse through the tubing into the air within the glass vial. Vapor-phase concentrations in the vial are typically reported in parts per billion by volume (ppb v).

In theory, these vapor concentrations can be converted to concentrations in water through Henry's Law and Henry's Law constants for specific chemicals. In practice, however, uncertainties about Henry's Law constants, pore-water temperatures, equilibration times for various types of sediments, and analytical precision, limit this application. If concentrations in water are needed, however, a modification of this approach, which is a single layer, water-filled membrane tubing sampler, will provide aqueous-phase VOC concentrations in a ground-water-discharge area (Vroblesky and others, 1999).

The ease of constructing, deploying, and retrieving PVD samplers renders this method well-suited for reconnaissance of VOC plumes discharging to surface waters. A large amount of spatial data can be collected in a short period with PVD samplers. For example,

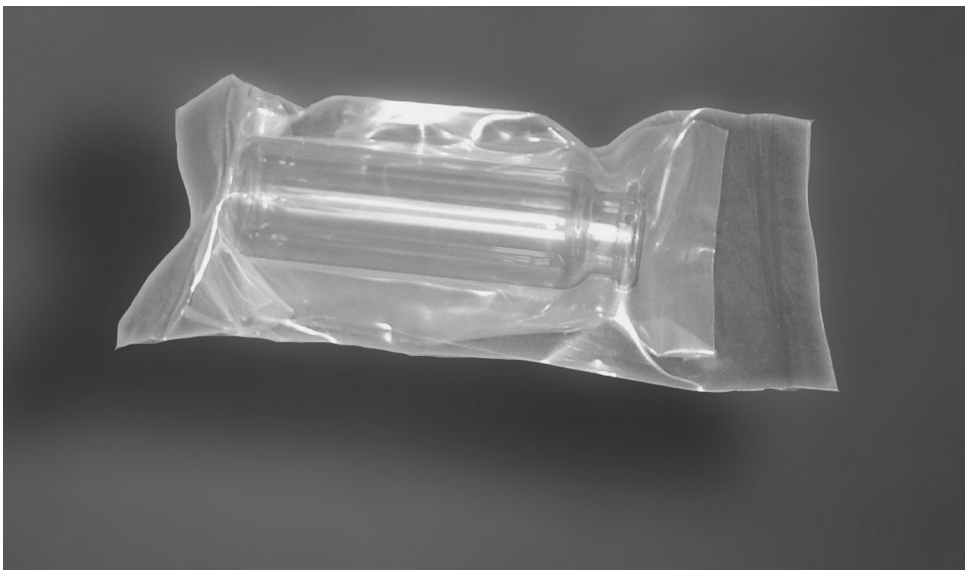

Figure 1. Glass vial in two layers of polyethylene tubing.

Table 1. Volatile organic compounds detected under field conditions with passive-vapor-diffusion samplers at contaminated ground-water-discharge areas in New England and South Carolina and the range of minimum reporting limits for these compounds at the nine New England sites

Volatile organic compound	Range of minimum reporting limits, in parts per billion by volume
Benzene	6 to 25
Ethylbenzene	40 to 90
meta/para-xylene	40 to 90
ortho-xylene	60 to 100
Toluene	20 to 40
Tetrachloroethene	5 to 25
Trichloroethene	5 to 25
Chlorobenzene	40 to 70
cis-1,2-Dichloroethene	25 (a target compound at only one site)
1,1,1-Trichloroethane	8 (a target compound at only one site)
methyl *tert* butyl ether	Not a target compound at the New England sites

from experience with PVD samplers in New England, construction of samplers, deployment of samplers in streambed sediments at 50 ft intervals along a 2,000 ft reach, retrieval of samplers after equilibration is reached (about two weeks), and on-site chemical analysis, may be accomplished in a total of three days. Results from this sampling may guide the placement of well points in shallow waters and monitoring wells or the selection of sediment-sampling locations where VOCs in water and sediments are detected. Once vapor concentrations of VOCs are detected with the PVD samplers, then water samples can be collected with other methods.

This report describes advantages and limitations of PVD samplers, offers guidance on the use of PVD samplers, and summarizes results from nine sites in New England where PVD samplers have provided useful information about VOC plumes in ground water. The report is designed mainly for personnel who are designing characterization studies that may include the use of PVD samplers and for personnel who will be constructing and installing the samplers. This report was prepared by the U.S. Geological Survey in cooperation with the U.S. Environmental Protection Agency (USEPA) Technical Innovation Office (TIO), and USEPA's Region I.

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ADVANTAGES AND LIMITATIONS OF PASSIVE-VAPOR-DIFFUSION SAMPLERS

Advantages and limitations are presented here, before the details of PVD-sampler assembly, deployment, and recovery are described, to ensure that project design personnel who may be considering or are planning to use PVD samplers understand capabilities of this method. These advantages and limitations may also be useful for technicians who assemble, deploy, and recover these samplers.

Advantages

1. The PVD method takes advantage of converging ground-water-flow lines and upward hydraulic gradients at ground-water-discharge areas to bring the target contaminants into contact with the samplers.
2. The method has been effective in delineating VOC-contamination-discharge areas beneath surface-water bodies.
3. PVD samplers can be areally and vertically distributed to gain information on contaminant-discharge heterogeneity.

4. The samplers are inexpensive. A low-cost sampler can be made from grocery-store sandwich bags and empty glass vials.
5. In many situations, the samplers are easy to deploy and recover.
6. Sampler recovery is rapid. The data can be analyzed on site with field gas chromatography, or the capped samples can be stored for later analysis. A stability test with 40-mL volatile organic analysis (VOA) vials showed that VOC concentrations in unpunctured, sealed vials did not substantially decrease in over 121 hours (Vroblesky and others, 1996).
7. Because the pore size of low density polyethylene tubing is about 10 angstroms or less, sediment does not pass through the membrane into the bag. The outer bag, therefore, effectively prevents contaminated soil from contacting the inner bag.
8. A variation of a PVD sampler can be used as a soil-gas sampler in unsaturated sediment to delineate shallow VOC plumes (Vroblesky and others, 1992). Vapor-filled polyethylene samplers also can be used with a sorbent to allow the samplers to accumulate VOC concentrations over the deployment period (Vroblesky and others, 1991). Still another variation consists of water-filled, low-density polyethylene tubing sampler deployed in bottom sediments at ground-water-discharge areas to yield aqueous concentrations of VOCs (Vroblesky and others, 1999).

Limitations

1. Because the change in VOC concentrations within PVD samplers in response to changes in ambient concentrations typically takes 24 hours or longer, VOC concentrations within the samplers represent an integration of concentrations from the most recent part of the deployment period until the samplers attain equilibrium. The equilibration time depends on several factors, including the temperature and the rate of water movement past the sampler. Under laboratory conditions, equilibration times in static water ranged from about 24 hours at 21°C to about 102 hours at 10°C. Under field conditions, equilibration times can range from as little as 12 hours in a rapidly discharging unconsolidated sand, to three weeks or more in colder, less permeable sediment. Suggested PVD deployment periods are typically two weeks, but may vary depending on site-specific temperature and hydraulic conditions. The required equilibration time is a disadvantage over some types of real-time sampling methods, such as extracting water from a core or pumping water from a small-diameter probe. Unlike these methods, however, the PVD samplers can provide an undisturbed sample, which minimizes the risk of short-term concentration changes from sediment disturbance and reduces the uncertainty associated with the source of water from a sample obtained from pumping.
2. The PVD samplers are appropriate only for volatile compounds.
3. Analysis of the samples requires a gas chromatograph.
4. Deployment of the samplers in shallow waters typically is a simple task; however, deployment in deep waters may require the services of SCUBA divers or other installation methods.
5. In some streams, the source of detected VOCs may not be readily determined without further work because of complexities in hydraulics and sediment heterogeneity that lead to unusual contaminant-discharge distributions. For example, in some streams of the Rocky Mountains region, where ground-water-flow direction is approximately parallel to streamflow, locations of ground-water-discharge areas can change with time. Furthermore, if the samplers are deployed in an area of VOC-contaminated bottom sediment derived from sediment transport along the stream, then the VOC concentrations in the PVD samplers may reflect contaminant concentrations in the sediment rather than in discharging ground water. Consequently, an effort should be made to ensure that the sampling location is a gaining reach.
6. The samplers must be deployed in an area where ground water is discharging to surface water to adequately reflect ground-water concentrations. In areas where the water in contact with the PVD samplers is largely infiltrated surface water, the concentrations detected by the PVD

samplers probably will represent surface-water or sediment-contaminant concentrations rather than ground-water concentrations.

7. Transient flow of ground water, such as bank storage after a flood wave or tidal cycle, may cause temporary or cyclic changes in concentrations of VOCs that could affect interpretations about the extent and concentration level of VOCs in ground water.
8. Follow-up studies that use other sampling methods are needed to determine actual concentrations of VOCs in water, if that is a goal of the study. The PVD samplers provide VOC concentrations as a gas. Because the partition between aqueous and vapor phases depends on several factors, such as temperature and pressure, which may vary from site to site and are not always known, calculations of aqueous-phase concentrations from PVD samplers should be considered estimates. An alternative approach to obtaining aqueous-phase VOC concentrations in a ground-water-discharge area is to use a water-filled, low-density polyethyene sampler as described elsewhere (Vroblesky and others, 1999).
9. Caution should be used when deploying PVD samplers in streambeds subject to rapid erosion, because the samplers may be washed away. Samplers also may be difficult to find when the surveyor flags are submerged in high flows in streams or buried beneath sediment as flows recede.

PART 1. GUIDANCE ON THE USE OF PASSIVE-VAPOR-DIFFUSION SAMPLERS

By Don A. Vroblesky

This section of the report provides guidance on PVD-sampler assembly, deployment, and recovery to detect volatile organic compounds in ground-water-discharge areas. As an aid to ensure proper use of this method and interpretation of the data collected, factors affecting PVD-sampler deployment, data interpretation, and quality control and assurance, are also discussed.

ASSEMBLY OF SAMPLERS

Several approaches may be used to construct a PVD sampler. A vial may be enclosed in "lay-flat," low-density polyethylene (LDPE) tubing, flexible tubing that is laid flat and wound-up in a roll, and then heat-sealed at both ends, or the vial may be enclosed in zipper-type sealable sandwich bags (fig. 2). The vials should be glass and sealable with a septated cap. Typical vials used include 20-mL crimp-top glass vials and 40-ml volatile organic analysis (VOA) glass screw-top vials. Vials used in the studies summarized in this report are 40-mL VOA screw-top vials. When the 20-mL crimp-top glass vials are used, 2-, 3-, or 4-mil LDPE may be used for the bag material. When 40-mL VOA vials are used, 2- or 3-mil LDPE for the inner material is advised, because the cap is difficult to screw onto 4-mil LDPE. The septum for the cap should be Teflon or Teflon coated. The effort for constructing PVD samplers is approximately equivalent for the two methods. Also, the material costs differ little between methods, except for the initial purchase of a heat sealer if constructing samplers with tubing. The LDPE tubing, however, is more resilient to punctures and abrasion during placement and retrieval, and is therefore preferred to construction with sandwich bags, particularly for placement in coarse gravels.

To construct a PVD sampler from lay-flat LDPE tubing and a heat sealer, the following supplies are needed: 2-in. wide (approximately 1.5-in. diameter), 2-, 3-, or 4-mil lay-flat LDPE tubing; a glass vial, a wire surveyor flag, self-locking nylon ties, and a heat sealer. The following approach describes a typical PVD-construction sequence.

1. Cut an 8-in. length of 2-in. wide lay-flat LDPE tubing. The inner layer of tubing should be 2- or 3-mil thick when VOA vials are used and 2-, 3-, or 4-mil when crimp-top serum vials are used. For the studies summarized in this report, 40-mL VOA screw-top vials were used.
2. Heat-seal one end. The heat sealer should be adjusted to provide a uniform seal without melting through the LDPE. Multiple seals may be required with some heat sealers with less than 400 watts of impulse power.
3. Insert an uncapped empty 40-mL glass VOA vial or a 20-mL crimp-top serum vial into the tube. Store the cap in a clean environment away from the PVD samplers until the sample is recovered.

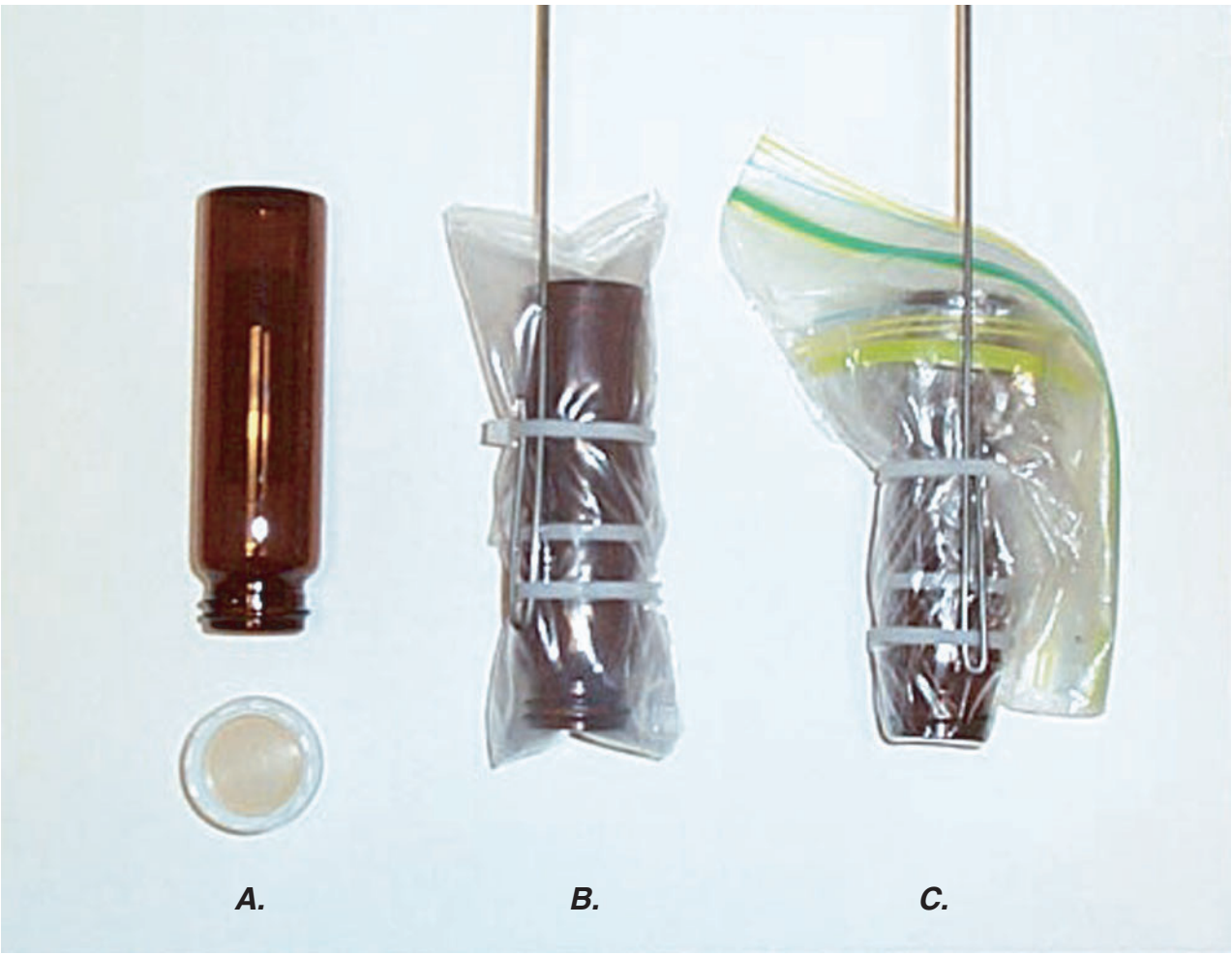


Figure 2. Passive-vapor-diffusion samplers with *(A)* vial and screw cap, *(B)* uncapped glass vial sealed in polyethylene tubing and secured to wire surveyor flag, and *(C)* glass vial sealed in polyethylene sandwich bags and secured to wire surveyor flag.

4. Remove the excess air space from the LDPE tubing. This can be accomplished by squeezing the LDPE tubing tightly against the vial or by twisting the tubing to tighten it against the vial.

5a. Position the unsealed end of the bag across the sealing element of the heat sealer, so that the sealing element is as close as practical to the mouth of the enclosed vial without stretching the LDPE across the opening (fig. 3). The LDPE should not be folded or wrinkled where it crosses the heating element of the heat sealer. Seal the bag. Once the bag is sealed, trim off the excess LDPE tubing. In this method, the LDPE is not necessarily tight across the vial opening.

5b. An optional method to arranging the heat-sealed end of the inner LDPE tubing across the vial opening is to, after both ends of the tubing are sealed, pull the tubing over the vial opening and fold the heat-sealed end of the tubing against the glass vial. After folding, secure the folded tubing to the vial with a self-locking nylon tie in a place where it will not interfere with attaching a vial cap during sampler recovery. In this method, the LDPE should be tight against the vial opening. This method improves sampler integrity over the first method because it reduces the probability of accidentally cutting the inner LDPE while removing the outer LDPE during sampler recovery.

Figure 3. Heat sealing of glass vial in polyethylene tubing.

6. Once the inner LDPE tubing is secure, cut another 8-in. length of 2-in. wide lay-flat LDPE tubing. This tubing will constitute the outer layer, which will be removed during sampler recovery to prevent sediment from interfering with capping the vials.
7. Heat-seal one end. The heat sealer should be adjusted to provide a uniform seal without melting through the LDPE. Multiple seals may be required with some heat sealers with less than 400 watts of impulse power.
8. Place the glass vial enclosed in the inner layer of LDPE into the new LDPE tube.
9. Press the LDPE against the vial to remove the excess air space from the outer LDPE tubing. The lack of air space will reduce buoyancy and maintain a consistent vapor volume.
10. Position the unsealed end of the bag across the sealing element of the heat sealer so that the sealing element is as close as practical to the mouth of the enclosed vial. No folds or wrinkles should be present where the LDPE tubing crosses the heating element of the heat sealer. Seal the bag. Once the bag is sealed, trim off the excess LDPE tubing.
11. Attach a wire surveyor flag to the PVD sampler to aid in sampler recovery. A practical method of attachment is to use self-locking nylon ties. The ties are attached tightly enough so that the surveyor flag does not pull free from the sampler during sampler recovery. The vial is attached so that the vial opening is in the opposite direction of the surveyor flag (fig. 2). One approach is to allow approximately 2 in. of wire extending beyond the nylon tie. The 2 in. of wire is then bent back 180 degrees over the nylon tie and laid adjacent to the wire above the tie. Add another nylon tie to secure the bent part of the wire tight against the vial (fig. 2). By this method, the surveyor flag does not pull free from the sampler during retrieval. The widest practical spacing between nylon ties will reduce a tendency for samplers to rotate on the wire and become wedged in sediment during retrieval.

The following method details how to construct a sampler with sandwich bags instead of lay-flat tubing.

1. Place an uncapped empty glass vial in a zipper-type polyethylene sandwich bag. Store the cap in a clean environment away from the PVD samplers until sampler recovery.

2. Remove the excess air space from the bag to reduce buoyancy of the sampler when deployed. This can be accomplished by squeezing or rolling the bag around the vial. Seal the bag with the zipper.
3. Secure the bag around the vial opening by tightening a self-locking nylon tie below the vial opening so that the tie and the excess bag will not interfere with capping the vial. A single layer of LDPE should now be tight across the vial opening (fig. 4).
4. Place the glass vial enclosed in the LDPE bag into another sandwich bag. Remove excess air from the outer bag and seal it with the zipper.
5. Attach a wire surveyor flag to the PVD sampler to aid in sampler recovery. A practical method of attachment is to use self-locking nylon ties. The ties are attached tightly enough so that the surveyor flag does not pull free from the sampler during sampler recovery. The vial is attached so that the vial opening is in the opposite direction of the surveyor flag (fig. 2). One approach is to allow approximately 2 in. of wire extending beyond the nylon tie. The 2 in. of wire is then bent back 180 degrees over the nylon tie and laid adjacent to the wire above the tie. Add another nylon tie to secure the bent part of the wire tight against the vial (fig. 2). By this method, the surveyor flag does not pull free from the sampler during retrieval. The widest practical spacing between nylon ties will reduce a tendency for samplers to rotate on the wire and become wedged in sediment during retrieval.

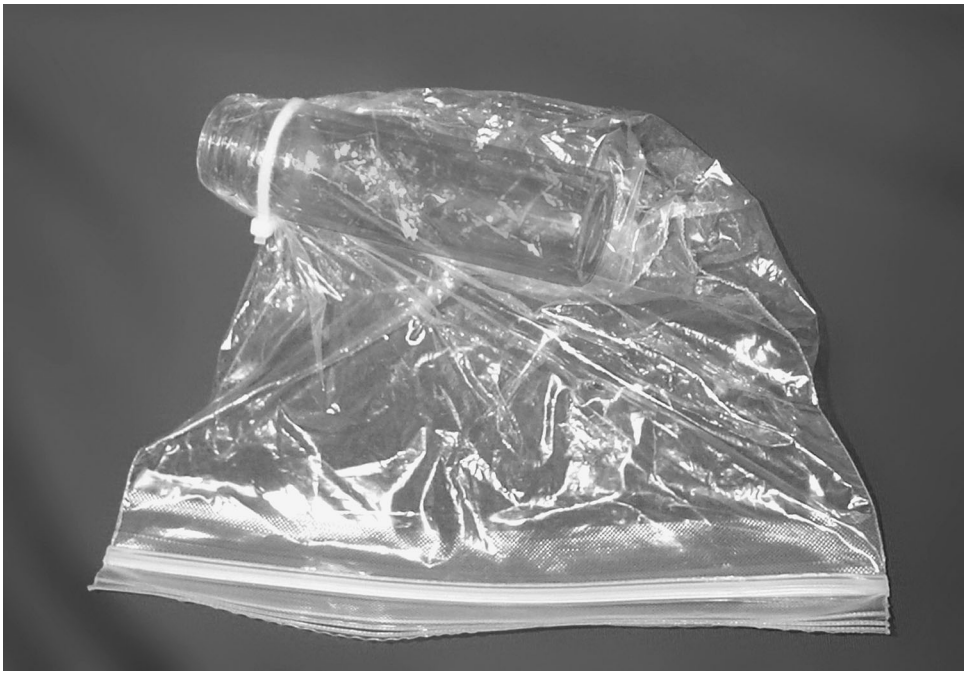


Figure 4. Glass vial positioned in sandwich bag so that a single layer of low-density polyethylene is tight across the opening and the self-locking nylon tie does not interfere with capping.

DEPLOYMENT OF SAMPLERS

Effective use of the samplers to delineate discharging contaminated ground water requires that samplers be deployed in ground-water-discharge areas. Many approaches have been used to identify gaining reaches of streams (zones where ground water discharges to surface water). To verify that the target section of the surface water is a gaining reach, install a streambed piezometer. In its simplest form, a streambed piezometer can be a pipe driven a few feet into the bed sediment. A bolt loosely fitted into the bottom of the pipe before installation can prevent sediment from moving into the pipe. After deployment a narrow rod then can be used to drive out the bolt to allow water to enter the pipe. After stabilization, comparison of ground-water-head measurements within the piezometer to surface-water stage outside the piezometer can indicate whether the head gradient is upward (gaining reach) or downward (losing reach). With this method, care should be taken to avoid a clogged pipe or a pipe with a leaky connection to surface water along the annular space between pipe and streambed sediments.

Many other methods have been used to identify areas of upwelling ground water beneath surface water. Near-shore discharge through a lakebed has been estimated with seepage devices (Lee, 1977) and hydraulic potentiomanometers (Winter and others, 1988). In areas where temperature differences between ground water and surface water are greater than normally expected, surface-water-temperature measurements and aerial infrared photography have been used to identify areas of ground-water discharge to streams (Silliman and Booth, 1993), lakes, and wetlands (Olafsson, 1979; Lee, 1985; Lee and Tracey, 1984; Baskin, 1998). Discharge areas of ground water to lakes sometimes can be located by towing temperature and specific-conductance probes from a boat (Lee, 1985). Researchers also have used the distribution of aquatic plant species as indicators of ground-water discharge to fens (Glaser and others, 1981; 1990; Verhoeven and others, 1988; Wassen and others, 1989), to saline wetlands (Swanson and others, 1984), and to a lake (Rosenberry and others, 2000).

Even within gaining reaches of a stream, the distribution of contaminant discharge can be complex. After storms, ground-water discharge may be dominated by release of bank storage. This transient flow may temporarily mask contaminated ground-water discharge.

Deployment of PVD samplers involves burying of samplers in the bottom sediment of a surface-water body. Ideally, the samplers should be buried at the bottom of the transition zone from surface water to ground water to ensure that the sample collected represents VOCs in ground water. Delineating the transition zone, however, often is difficult, and holes dug beneath the water tend to rapidly refill with sediment. Samplers placed at shallow depths (for example, 0 to 0.5 ft) may be within this transition zone and samples may be affected by surface water. Samplers placed at shallow depths may also become dislodged. Samplers placed at greater depths (for example, greater than 1.5 ft) may be below the transition zone, but also may be difficult to retrieve. The most effective depths of sampler deployment may vary spatially and with time, and are dependent on many factors, including hydraulic conductivities of the sediments and hydrologic conditions. With the deployment method described, a practical target depth is between 0.5 and 1.5 ft. Deployment depths are described in detail more in the section "Factors Affecting Deployment of Samplers and Data Interpretation."

In shallow waters, waters up to 2 ft deep, where the samplers can be installed with hand augers or shovels (fig. 5), one approach to digging the hole is to shovel the sediment until the likelihood of hole collapse makes further digging impractical. At that point, insert the shovel into the sediment and push forward to create an opening between the back of the shovel and the sediment. In more cohesive sediment, the hole can be excavated with a hand auger. Exercise care during insertion of the PVD sampler into the hole to prevent rupturing of the polyethylene membrane covering the vial opening. Backfill the hole with the inserted PVD sampler with the sediment removed from the hole. Ensure that the hole has been adequately backfilled above the sampler to minimize entrainment of the top-most sediment layer above the PVD sampler to the bottom of the hole. To reduce the potential for contamination from sample-labeling pens, label the surveyor flag either several days before PVD-sampler construction (to allow vapors from water-proof markers to dissipate) or after the sampler is buried.

Figure 5. Installation method for passive-vapor-diffusion samplers in water 0 to 2 feet deep. *(A)* passive-vapor-diffusion sampler secured to wire surveyor flag and tools used for installation, *(B)* insertion of sampler in space behind flattened surface of steel bar driven into cobble bottom sediments, and *(C)* passive-vapor-diffusion sampler installed.

In water deeper than about 2 ft, manual insertion of a sampler in a hand-augered hole or behind a shovel blade is not practical in conventional wading gear (hip or chest waders). A drive-point assembly has been effective in water 2 to 4 ft deep where chest waders are needed. The drive-point assembly has also been used from a row boat (Campbell and others, 2002) and through an ice cover (Lyford and others, 2000; Church and others, 2002) to install samplers in soft bottom sediment at depths to about 7 ft. Greater depths of installation may be possible from a boat, barge, or through ice, but has not been attempted. The drive-point assembly and its application are illustrated in figures 6 and 7.

Drive-point assemblies can be constructed at various lengths to suit different needs. The drive-point assembly most commonly used in New England studies consists of a 72-in. long, 1 3/4-in. outside diameter (OD), 1 5/8-in. inside diameter (ID) electrical conduit outer pipe; a 74-in. long, 1 1/2-in. OD, 1 3/8-in. ID electrical conduit inner pipe; and an 80-in. long, 7/8-in. OD, 3/4-in. ID polyvinylchloride (PVC) pipe. A 2-in. OD pipe cap is attached to the top of the 1 1/2-in. inner pipe, and a 2-in. long steel point is flush-mounted to the bottom. The outer and inner pipes are driven into the bottom sediments by striking the pipe cap on the inner pipe with a sledge or slide hammer. At the desired depth of installation, the inner pipe is removed, leaving a hole in the sediment extending about 2-in. deeper than the bottom of the outer pipe. The surveyor flag end of the PVD sampler is then pushed into the PVC pipe to where it is stopped by the tubing of the sampler. The PVC pipe and attached sampler are then inserted and pushed through the outer pipe into the sediment. The sampler is held in place by the PVC pipe as the outer pipe is removed. Sediments then collapse around the sampler, and the PVC pipe is removed from the sediment.

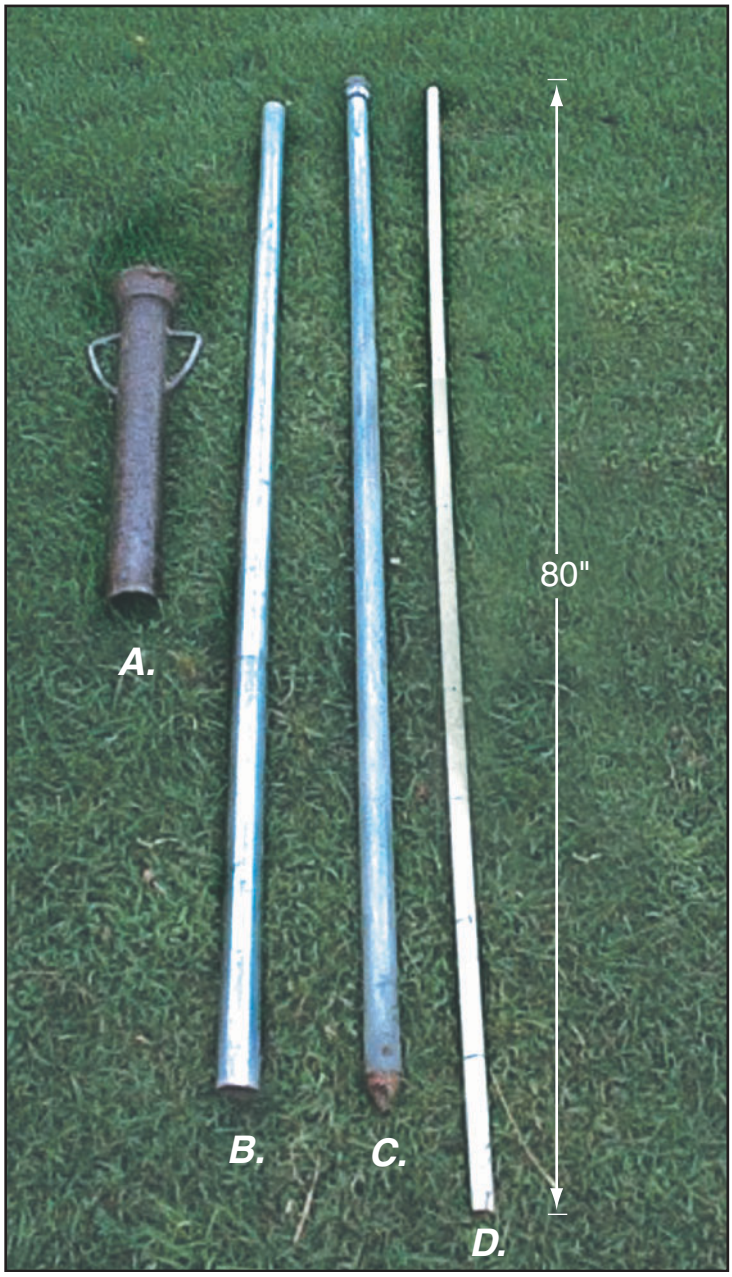


Figure 6. Drive-point assembly for installation of passive-vapor-diffusion sampler in water 2 to 4 feet deep in clayey silt to coarse sand and gravel sediments. (*A*) slide hammer, (*B*) 1 5/8-inch inside diameter steel electrical conduit, (*C*) 1 3/8-inch inside diameter steel electrical conduit with machined point, (*D*) polyvinylchloride sampler-insertion pipe.

Figure 7. Drive-point method for installation of passive-vapor-diffusion sampler in water 2 to 4 feet deep in clayey silt to coarse sand and gravel sediments. *(A)* 1 5/8-inch inside diameter (ID) steel electrical conduit with 1 3/8-inch ID steel insert conduit with 2-inch point driven into pond-bottom sediment with slide hammer, *(B)* insert pipe removed after driven to desired depth, *(C)* insertion of passive- vapor-diffusion sampler to polyvinylchloride (PVC) pipe (surveyor flag and wire inserted into pipe with sampler exposed), *(D)* insertion of PVC pipe with sampler into sediment through 1 5/8-inch ID steel conduit, *(E)* removal of 1 5/8-inch ID steel conduit, and *(F)* removal of PVC pipe leaving sampler installed in sediment.

At depths greater than 4 ft, divers may be needed to install PVD samplers. Divers have been used to install samplers in pond-bottom sediment to pond depths of 30 ft (Savoie and others, 2000). Divers inserted PVD samplers in soft sediment by hand and used a trowel in gravelly sediments.

For studies in New England, the samplers were found to be resistant to removal by high flows if buried to depths of 8 in. or greater into the sediment. Less than five percent of the approximate 1,250 samplers installed in the New England sites were lost. In a few instances, firmly planted samplers were not found when the surveyor wire flag broke free from the self-locking nylon ties upon retrieval, or when stream-channel sediment buried the flag.

RECOVERY OF SAMPLERS

The amount of time PVD samplers must remain deployed in the sediment before recovery is, in part, based on the data-quality objective of the study. If the objective is to identify the presence or absence of VOC(s), samplers could be recovered within a few days. Field studies suggest that this can be accomplished after a deployment period of 8 days or less, and as little as 24 hours in some environments. If the objective is to estimate the concentration(s) of VOC(s), samplers cannot be recovered until enough time for equilibrium has elapsed. As discussed earlier, several factors, such as hydraulic conductivity of streambed sediments, hydraulic gradients, and water temperatures, affect the amount of equilibration time needed. Field evidence, discussed in Appendix I, suggests that an equilibrium period of approximately 2 weeks is adequate for most investigations in sandy formations. Longer or shorter periods may be appropriate depending on water temperatures and hydraulic conditions. It is important to remember, however, that PVD samplers typically are deployed in sediments as a reconnaissance tool to locate areas where ground water contaminated with VOCs is discharging. For this use, determining the presence or absence of target VOCs may be sufficient to meet the data-quality objectives of the sampling. A recent study showed that within 24 hours in four separate streams, the recovered PVD samplers contained chlorinated aliphatic compounds from discharging ground water at concentrations well above detection limits, although the samplers had not yet equilibrated with the ground water concentrations at three of the sites (Vroblesky and Campbell, 2001).

Recovery of PVD samplers can be accomplished relatively rapidly. A 2-member team is needed; one person with “dirty hands” who retrieves samplers and touches the outer tubing only; the other person with “clean hands” who caps and stores samplers and touches the inner tubing only. A second clean hands person may be needed in situations where sets of samplers (10 or 20 samplers) are delivered to an on-site portable laboratory several times a day, and to assist in labeling and note taking. The specific recovery steps are listed below:

1. Pull the surveyor flag or excavate the sediment to remove the PVD sampler. Pull with a steady tension rather than a sudden forceful extraction that can cause nylon ties to break. Examine the sampler for integrity. Record unusual features, such as discoloring or water inside the outer bag. Discard or quickly cap and record a sampler with a ruptured inner seal.
2. Cut and remove the outer tubing or bag from around the vial opening. Do not pierce or cut the inner tubing or bag, because this can allow trapped vapors within the vial to escape or allow ambient air to enter, resulting in incorrectly low VOC concentrations within the vial. An alternative approach to removing the outer tubing that reduces the chance of puncturing the inner bag is to cut the outer nylon ties. After cutting the ties, use scissors to cut the end of the outer tubing adjacent the vial opening, and then push on the opposite end of the outer tubing to slide the sampler into the hands of the clean-hands person. Diagonal cutters (electrician’s pliers) are effective for cutting nylon ties that attach samplers to surveyor flags. Inspect the sampler and record any unusual features, such as discoloring or water inside the the inner bag. Discard or quickly cap and record a sampler with a ruptured inner seal.
3. Cap the vial by screwing (fig. 8) or crimping (fig. 9) a cap onto the vial to seal the inner tubing or bag over the vial opening. Use caps that have a Teflon or Teflon-lined septum to allow sampling by syringe.

4. Label the vial after capping if the vial is removed from the labeled surveyor flag. The inner tubing or bag may be cut around the bottom of the cap and removed to facilitate labeling.
5. Store the PVD samplers away from any potential VOC-contaminant sources and in a chilled environment (4°C; ice or refrigerator), to reduce VOC leakage. If the vapor in the sampler is to be analyzed immediately, chilled storage is not needed.

The vapor sample obtained from the recovered PVD sampler can be analyzed on site with a gas chromatograph. Guidance on the use of a gas chromatograph is described in Appendix 2.

Figure 8. Screwing a septated cap onto a glass vial encased in the inner low-density polyethylene tubing.

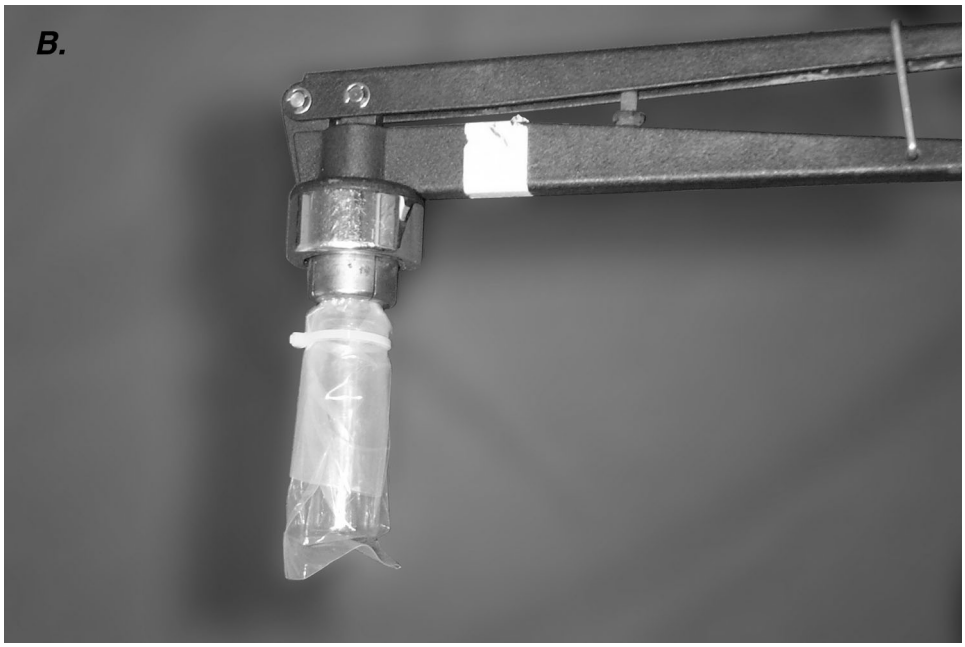


Figure 9. *(A)* Attaching and *(B)* crimping a septated cap onto a glass vial encased in the inner low-density polyethylene tubing.

FACTORS AFFECTING DEPLOYMENT OF SAMPLERS AND DATA INTERPRETATION

The effectiveness of PVD samplers as a reconnaissance tool to detect discharge areas of VOC-contaminated ground water depends on a variety of factors affecting contaminated ground-water discharge. Understanding these factors will help in selecting optimal sampler-deployment locations and will aid in data interpretation.

Aquifer and streambed lithologic heterogeneity affects discharge complexity and the optimal sampler-deployment locations. Using PVD samplers, Lyford and others (1999a) found that an irregular pattern of trichloroethene discharge to the Royal River, Maine, was related to the lithologic heterogeneity of the aquifer and riverbed sediments, and that significantly higher concentrations of contaminants discharged at sand boils. Conant (2000) found that contaminant discharge to a river in Ontario was predominantly associated with local gaps in the semi-confining unit beneath the river. Discharge of ground water beneath lakebeds can be particularly difficult to investigate because the water can discharge at low rates over a large area, and both rate and area can change with time. Winter (1976, 1978) has shown that the discharge is controlled predominantly by the spatial distribution of heads and hydraulic conductivity in the aquifer, as well as the bathymetry and sediment type of the lake bottom.

Another factor affecting contaminant discharge to rivers is the orientation of the river relative to the flow direction of the ground-water contamination. An investigation in Greenville, South Carolina, showed that reaches of a stream that were at a sharp angle to the axis of contamination-plume migration received greater contaminant discharge than reaches oriented approximately parallel to the direction of contaminant transport (Vroblesky, 2000). In a channel meandering through a tidally flooded wetland, the highest concentrations of discharging contaminants were found where the meander approached the shoreline that contained the ground-water contamination (Vroblesky and Lorah, 1991). This area was the most probable contaminant-discharge area because of its proximity to the ground-water contamination, and because the stream reach was oriented approximately perpendicular to the ground-water-flow path. Particular effort, therefore, should be exercised during sampler deployment in sediment beneath a meandering stream to ensure adequate density of sampling locations in reaches where the stream is oriented at sharp angles to the contaminant transport direction. Similarly, care should be exercised in wetlands to adequately target zones where channel meanders approach the shoreline that contains the ground-water contamination.

When deploying samplers in lakes or large streams, consideration should be given to the depth of the contaminant plume as it approaches the surface-water body. Knowing this depth will help estimate the probable distance of contaminant discharge from the shoreline. In thick aquifers, there is often a deeper flow system beneath shallow stream subsystems (Toth, 1963). Thus, contaminant discharge from a distant source, which travels in the deep aquifer system, will discharge into the surface-water body at a greater distance from the shoreline than nearby contaminants that travel in a shallower flow system. Savoie and others (2000) found that contaminants emanating from a source approximately 1.5 miles upgradient from the shoreline of a kettle pond discharged into the pond 100 to 350 ft offshore. A second previously unknown plume was detected discharging into the pond at a distance of 25 to 200 ft offshore (Savoie and others, 2000). Samplers deployed near the shore would not have detected these plumes.

Similar considerations for placement of PVD samplers should be given to deployment in streams. In an ideal gaining stream with homogeneous bottom sediment and similar ground-water hydraulic gradients on both sides of the channel, ground water moving beneath a particular shoreline typically discharges to the stream closer to that shoreline than to the opposite shoreline. In this case, VOCs detected near a particular shoreline probably came from ground water derived in the upgradient direction of that shoreline. The lithologic and hydrologic complexities of streams, however, can create complex discharge pathways, sometimes making it difficult to select optimum-sampler placement sites and to identify contaminant-source directions.

Temporal changes in the locations of discharge areas also can affect concentrations of VOCs in discharge and affect interpretation of data from PVD samplers. A study of a small Coastal Plain stream in South Carolina to which petroleum hydrocarbons were

discharging showed that the stream contained an upstream gaining reach and a downstream losing reach. The boundary between the two reaches migrated upstream during periods of low ground-water levels and streamflow and downstream during periods of high ground-water levels and streamflow (Vroblesky and others, 1997). Thus, PVD samplers placed near the gaining/losing boundary in this stream can be expected to intercept upward moving ground water during part of the year and downward moving surface water during a different part of the year. Additional temporal variations in contaminant discharge through a streambed have been observed following nearby well construction (Vroblesky and Robertson, 1996).

Because the VOC concentration within a PVD sampler represents an equilibrium between the vapor phase in the sampler and the adjacent aqueous solution, changing aqueous-contaminant concentrations produce a corresponding change in the vapor-phase concentrations. If PVD samplers in a local area are removed sequentially over time following an equilibration period, they can be used to track temporal changes in the contaminant concentrations of discharging ground water (Vroblesky and Robertson, 1996). Because PVD samplers are sensitive to temporal fluctuations, samplers for a particular sampling event should all be collected sequentially within a few hours of each other to obtain a "snapshot" of the contaminant-discharge distribution.

The depth to which the samplers are installed also may affect the results. The samplers should be installed at or below the ground-water/surface-water interface; however, the location of the interface typically is difficult to delineate. It may be at the sediment/water interface or at some depth below the sediment. In some areas, the interface may shift as a result of daily or seasonal fluctuations in river stage and ground-water flow. Surface water may enter the sediment at the head of riffles and dropoffs and re-enter the river at the upstream edge and base of pools (Vaux, 1968; Boulton, 1993). The surface water also can leave the channel laterally and travel through the streambanks before eventually re-entering the channel downstream (Harvey and Bencala, 1993). The movement of surface water into bed sediments is more pronounced in high permeability sediment than in low permeability sediment; therefore, PVD samplers buried in shallow sandy horizons in these zones may intercept local surface water rather than discharging ground water. Contaminated ground water upwelling beneath these zones may be diverted and discharge farther downstream (Conant, 2000). For practical reasons, PVD samplers often are buried at a uniform depth of approximately 0.5 to 1.5 ft, which may or may not be below the ground-water/surface-water interface. It is important, therefore, to consider the implications of subsurface streamflow when interpreting the PVD-sampler data.

Furthermore, if the samplers are deployed in an area of VOC-contaminated bottom sediment derived from sediment transported in the stream, then the VOC concentration in the PVD samplers may reflect contaminant concentrations in the sediment rather than in discharging ground water. It is important, therefore, to consider the possibility of stream transport of contaminated sediment when interpreting PVD data. In some cases, this situation probably can be resolved by deploying the samplers beneath such sediment.

An additional factor affecting data interpretation and sampler deployment is the potential for removal of the target compounds by micro-organisms in the sediment. The large diversity of micro-organisms and oxidation reduction conditions commonly found in wetland sediments may lower contaminant concentrations locally. Consequently, PVD samplers buried beneath the organic-rich bed sediments may detect a substantially higher concentration of VOCs than samplers placed in the upper part of the organic-rich sediment. In this situation PVD samplers can help evaluate VOC loss over a particular interval.

QUALITY CONTROL AND ASSURANCE

The primary purpose of most studies that use PVD samplers is to determine or verify the presence of VOCs. Relative concentrations of VOCs detected at the site are also of interest. Variability and bias introduced during sample collection, however, affects the interpretation of the results. Confidence in the detections and the relative concentrations of VOCs in samples collected with PVD samplers can be evaluated by collecting a series of quality-control (QC) samples, such as duplicate, trip, and equipment-blank samples.

Duplicate or co-located samples provide information needed to estimate the precision of concentration values affected by the combination of uncertainties associated with field variability, sample processing, and the analytical method. A duplicate PVD sampler consists of two separate samplers deployed adjacent to each other in the same hole. These samplers are typically held together side-by-side to the same surveyor flag with nylon ties to ensure that the open end of the vials are at the same depth. To account for sampler variability, at least 10 percent of the samplers should be duplicates. Examples from studies in New England show that a VOC was detected in 1 of the duplicate samples but not in the other in only about 2.5 percent of the 437 duplicate samples. The relative percent difference (RPD) between VOC concentrations in the 83 duplicate samples where a VOC was detected in both samples ranged from 0 to nearly 200 percent. About 75 percent of these RPDs, however, were less than 30 percent, which is a reasonable range for a reconnaissance tool. Duplicate samplers also can provide a backup in case one of the samplers is compromised.

Trip blanks are PVD samplers that are prepared offsite, typically with construction of all the samplers expected to be used at the site. They are stored and transported to the sampling location with the other PVD samplers and capped at the sampling location when the PVD samplers are deployed. The trip blanks are then stored with other samples as they are recovered, and analyzed with the recovered samples. A positive detection in the trip blank means that the PVD samplers were exposed to specific contaminant(s) sometime before deployment. To some extent, this detection imparts a degree of uncertainty to the detections of that specific compound in the recovered PVD samples. It should be noted, however, that the samplers re-equilibrate to their surroundings. If background samples do not contain the specific contaminant, then it is highly probable that sufficient deployment time elapsed to allow concentrations of the specific contaminant to re-equilibrate to ambient conditions in all of the deployed samplers.

Some of the PVD samplers should be deployed in an area of the surface-water body considered to be away from potential VOC contamination, such as upstream in rivers. If contaminants are found in samplers from a target area, but not in the background samplers, then this provides increased confidence that the contaminants are not an artifact of the methodology.

PART 2. EXAMPLE APPLICATIONS IN NEW ENGLAND

During 1996 through 2000, PVD samplers were used at nine Superfund sites in New England to identify likely discharge areas for VOCs in ground water (fig. 10). These sites were selected for study because contamination of ground water by VOCs was known or suspected. The sites represent a variety of hydrologic settings including rivers, streams, ponds, wetlands, and coastal shorelines (table 2). Samplers, all constructed by methods described in Vroblesky and others (1996), were placed in sediments ranging from clayey silt to cobbles. Vapor concentrations in samplers ranged from not detected to more than 1,000,000 parts per billion by volume (ppb v). The principal VOCs detected include the chlorinated compounds tetrachloroethene (PCE), trichloroethene (TCE), and chlorobenzene, and the petroleum compounds benzene, ethylbenzene, *meta-para*-xylene, *ortho*-xylene, and toluene. At all nine Superfund sites, discharge areas of known ground-water plumes contaminated with VOCs were confirmed and refined with PVD samplers. At four of these sites, results of PVD sampling has lead to the identification of previously unknown plumes of contaminated ground water and has helped guide further characterization of ground water at these sites. The following sections briefly describe each of the nine study areas, state the purpose and design of PVD sampling, present sampling results on maps, and summarize findings. Also included is a summary of the quality control and assurance results for the nine studies. These summaries were extracted from published reports. Additional detail about any of these studies can be found in the cited reports.

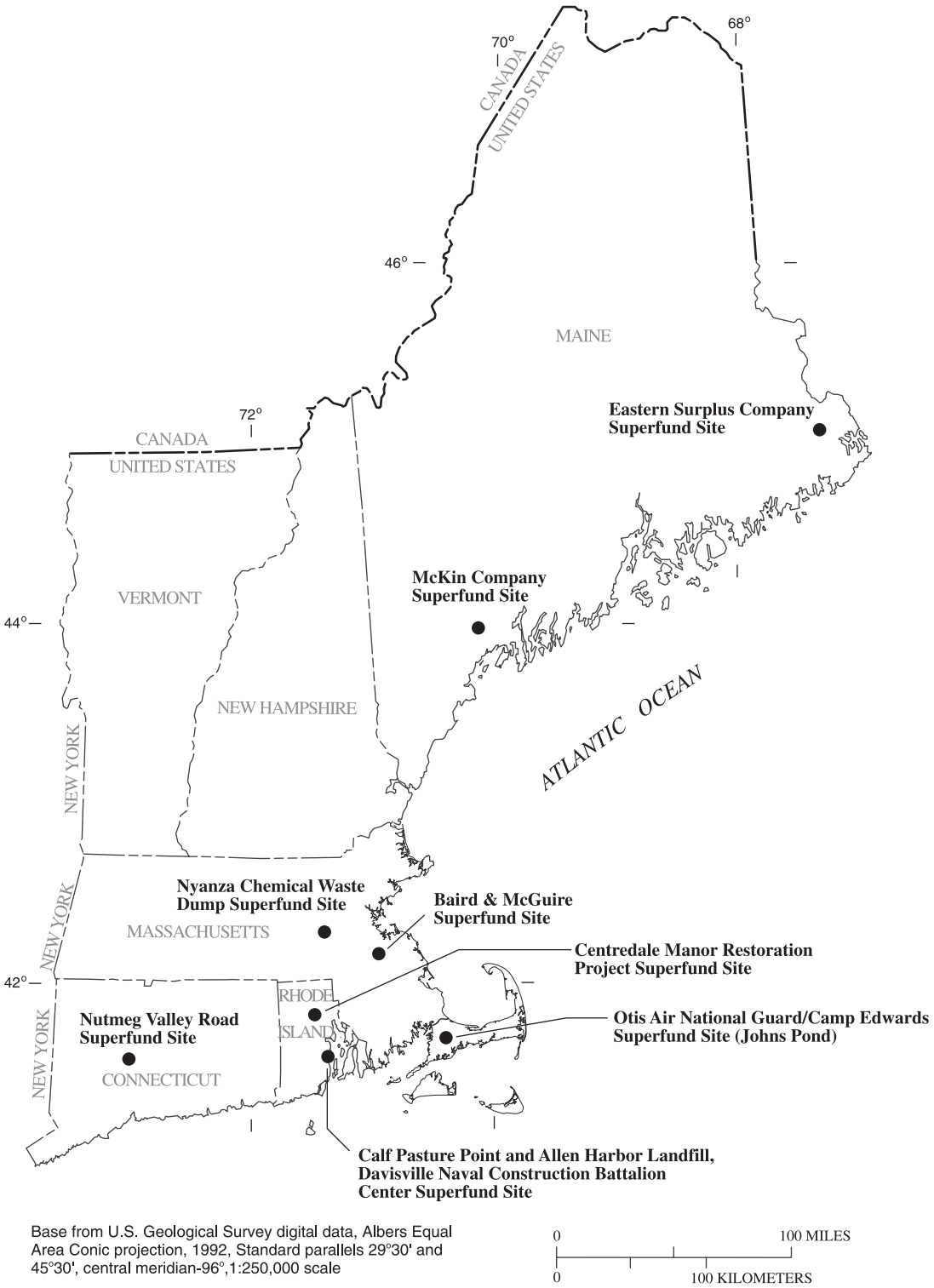


Figure 10. Locations of sites in New England where passive-vapor-diffusion samplers have been used to detect and delineate discharge areas of ground water contaminated by volatile organic compounds into surface-water bodies.

Table 2. Superfund sites in New England where passive-vapor-diffusion samplers were used to detect and delineate volatile organic compounds in bottom sediments of surface-water bodies, hydrologic setting, principal compounds detected, and maximum vapor concentration measured

[Concentrations in parts per billion by volume. PCE, tetrachloroethene; TCE, trichloroethene; petroleum compounds, (benzene, toluene, ethylbenzene, *meta/para*-xylene, and *ortho*-xylene)]

Site	Hydrologic setting	Principal compound(s) detected	Maximum vapor concentration measured
Eastern Surplus Company Superfund Site, Meddybemps, Maine	Lake and river	PCE	240
		TCE	70
		Toluene[1]	2,500
McKin Company Superfund Site, Gray, Maine	River	TCE	30,400
Nutmeg Valley Road Superfund Site, Wolcott and Waterbury, Connecticut	River	TCE	> 30,000
Baird & McGuire Superfund Site, Holbrook, Massachusetts	River	Petroleum compounds	216,000
		TCE + PCE	1,900
Allen Harbor Landfill, Davisville Naval Construction Battalion Center Superfund Site, North Kingstown, Rhode Island	Coastal shoreline	TCE	340,000
		PCE	1,700
		Benzene	940
Calf Pasture Point, Davisville Naval Construction Battalion Center Superfund Site, North Kingstown, Rhode Island	Coastal shoreline and wetland area	TCE (shoreline)	1,900
		TCE (wetland)	14
Otis Air National Guard/Camp Edwards Superfund Site, Johns Pond, Falmouth, Massachusetts	Pond	TCE	47,000
		PCE	667
Nyanza Chemical Waste Dump Superfund Site, Ashland, Massachusetts	River, former mill raceway, and pond	Chlorobenzene	5,330
		TCE	1,910
Centredale Manor Restoration Project Superfund Site, North Providence, Rhode Island	River and former mill raceway	PCE	1,390,000
		TCE	182,000

[1]May have been derived from adhesive tape used to secure polyethylene membrane to glass vial.

EASTERN SURPLUS COMPANY SUPERFUND SITE, MEDDYBEMPS, MAINE

By Forest P. Lyford *and* Edward M. Hathaway

Description of Study Area

The Eastern Surplus Company in Meddybemps, Maine, was a retailer of surplus and salvage items from 1946 until 1985. Activities at the site caused the release of chemicals, including VOCs and polychlorinated biphenyls (PCBs), to the environment (E.M. Hathaway, U.S. Environmental Protection Agency, written commun., 1996). The Eastern Surplus Company Superfund site (Eastern Surplus site) covers about 4 acres adjacent to Meddybemps Lake and the Dennys River, which flows from Meddybemps Lake (fig. 11). Surficial materials in an approximately 30-acre study area that encompasses the site vary widely in texture. Materials include till at the northern end and on the eastern side of the Dennys River, coarse sand and gravel on the western side, silt deposited in a marine environment in the central part of the site, and marine clay over coarse materials and till on the southern side. Surficial materials are generally less than 30 ft thick. In some areas, these materials lie above the water table for all or much of the time. Ground water in surficial materials under the site generally flows toward the Dennys River (fig. 12). Bedrock includes diorite and granite where ground water moves in fractures. Ground water in bedrock under the site generally flows eastward toward Meddybemps Lake at the northern end of the site and southward to eastward toward the Dennys River elsewhere (fig. 12) (Lyford and others, 1998). Some ground water flows toward a depression in the bedrock potentiometric surface caused by pumping for residential use on the southeastern side of the study area.

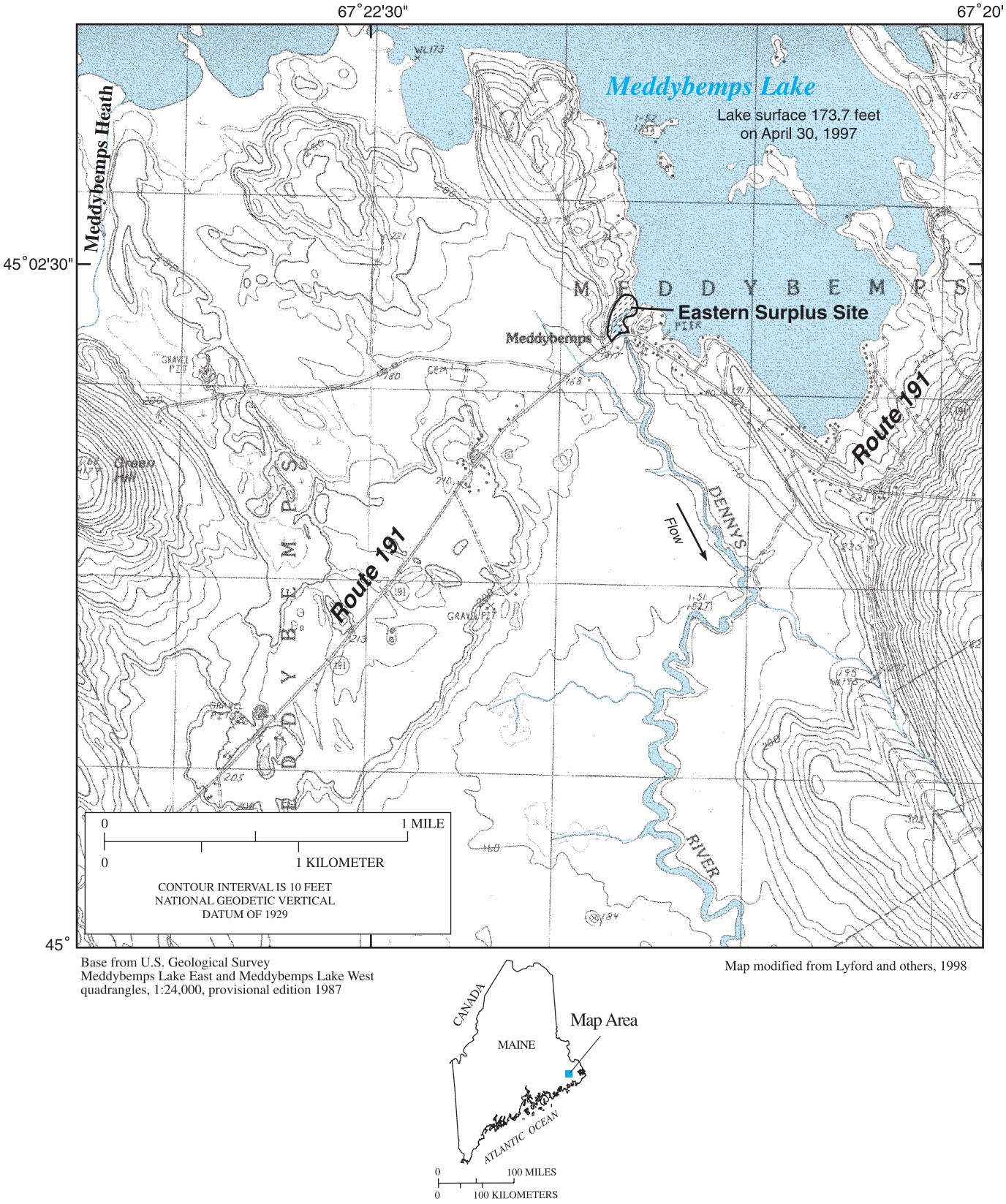
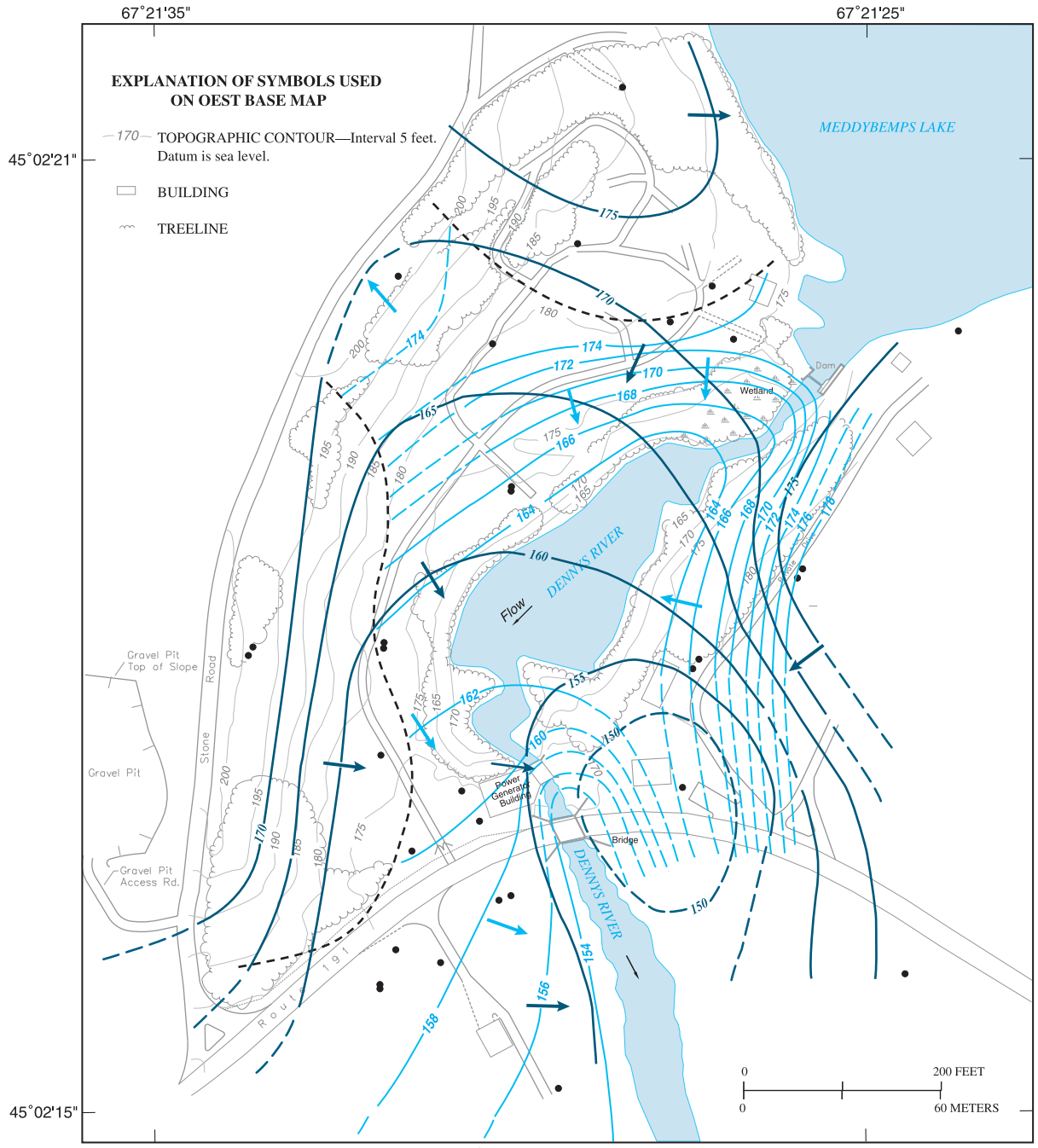


Figure 11. Location of the Eastern Surplus Superfund Site and study area, Meddybemps, Maine.



Base map modified from OEST Assoc. Inc., 1997

EXPLANATION

170 WATER-LEVEL CONTOUR IN SURFICIAL AQUIFER—Shows altitude at which water would have stood in tightly cased wells completed in the surficial aquifer, April 30, 1997. Dashed where approximately located. Contour interval is 2 feet. Datum is sea level. (Lyford and others,1998)

170 WATER-LEVEL CONTOUR IN BEDROCK—Shows altitude at which water would have stood in tightly cased wells completed in bedrock, April 30, 1997. Dashed where approximately located. Contour interval is 5 feet.

EXTENT OF SURFICIAL AQUIFER—Marks western and northern extent of area where saturated surficial materials are generally thicker than 2 feet.

GENERAL DIRECTION OF WATER FLOW
Surficial aquifer
Bedrock aquifer

MONITORING WELL

Figure 12. Potentiometric surfaces and generalized ground-water-flow directions for the surficial and bedrock aquifers, Eastern Surplus Superfund Site, Meddybemps, Maine, April 30, 1997.

Purpose and Design of Sampling

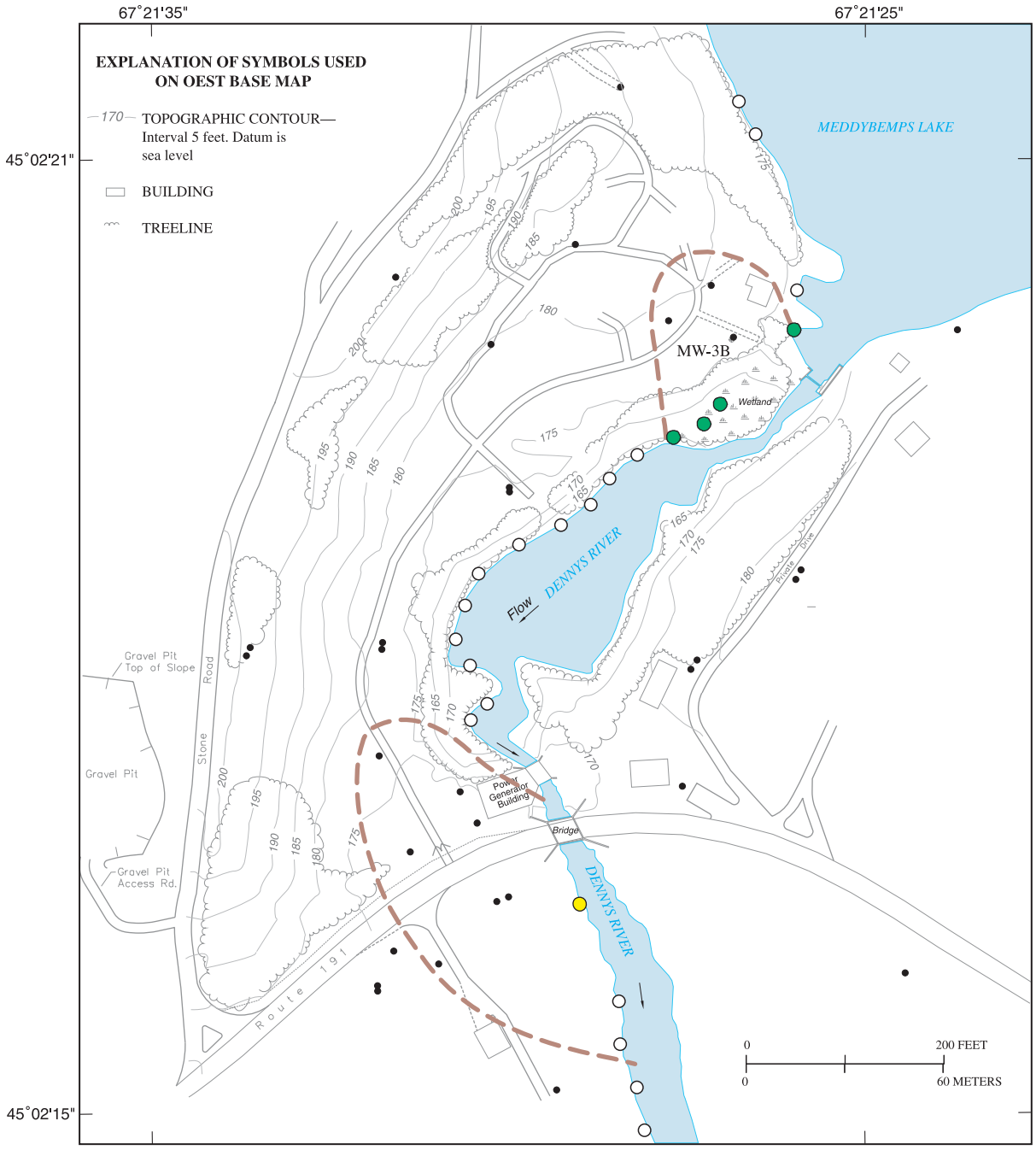
Sampling of four monitoring wells in 1988 identified one area at the northern end of the site, near well MW-3B, where PCE and TCE were present in ground water in fractured bedrock (E.M. Hathaway, written commun., 1996) (fig. 13). Ground-water sampling points were limited, and other areas of ground-water contamination were possible. During early phases of a study by the USGS in 1996-97, PVD samplers were placed along the shore of Meddybemps Lake and the west bank of the Dennys River to determine if other VOC plumes were present and discharging to surface water (Lyford and others, 1998).

To our knowledge, the use of PVD samplers at the Eastern Surplus site was the first application in New England. Sampler construction included the use of adhesive tape to hold the polyethylene membranes firmly to bottles. Samplers were placed about 25 to 50 ft apart along most of the shoreline and river bank (fig. 13). Very coarse materials consisting of cobbles and boulders along the shoreline and river bank precluded the installation of samplers in some areas. During this early attempt to use PVD samplers, the most effective method found for installation in the coarse materials was by manual insertion in a hole formed behind a shovel driven into bottom materials and forced forward. The PVD samplers were in place for about one month before retrieval and on-site analysis of vapors.

Results

The VOCs detected in PVD samplers included PCE, TCE, and toluene. The compounds PCE and TCE were detected near well MW-3B, where they had been detected in ground water (fig. 13). The sample from one sampler placed along the Dennys River south of the site also contained PCE and TCE. Subsequent installation of monitoring wells and ground-water sampling in this area identified a previously unknown plume of VOCs, mainly PCE, in surficial materials and bedrock. The plume appeared to originate at the southern end of the site (Lyford and others, 1998) (fig. 13). The extent of this plume, shown on figure 13, is based on water samples from wells that were installed after the survey with PVD samplers.

Toluene was detected in several PVD samplers but not in water from monitoring wells. The toluene may have been derived from the adhesive tape used to secure the surveyor flag and tubing to the glass vials. Similar occurrences of toluene in diffusion samplers wrapped with adhesive tape were described by Mullaney and others (1999).



Base map modified from OEST Assoc. Inc., 1997

EXPLANATION

EXTENT OF TETRACHLOROETHENE AND TRICHLOROETHENE IN GROUND WATER—Shows the extent of concentrations greater than 5 micrograms per liter.

PASSIVE-VAPOR-DIFFUSION SAMPLERS—Shows concentrations of tetrachloroethene and trichloroethene in parts per billion by volume (ppb v).

- Greater than 100 to 1,000
- Trace to 100
- Not detected above reporting limit of 40 ppb v or at trace level

MONITORING WELL

Figure 13. Concentrations of tetrachloroethene (PCE) in passive-vapor-diffusion samplers installed in river-bottom sediments on the western edge of Dennys River, Meddybemps, Maine, October 1996.

McKIN COMPANY SUPERFUND SITE, GRAY, MAINE

By Forest P. Lyford, Terrence R. Connelly, *and* Laura E. Flight

Description of Study Area

The McKin Company Superfund Site (Mckin site) in Gray, Maine, is a former waste-collection, transfer, and disposal facility that operated from 1965 to 1978. Some of the wastes, including petroleum hydrocarbons and chlorinated solvents, infiltrated and contaminated ground water. A contaminant plume in ground water, consisting mainly of TCE, extends northward and eastward from the site for several thousand feet (fig. 14). The eastern plume discharges to the Royal River in an area known locally as Boiling Springs (Sevee and Maher Engineers, Inc., 1999). Since at least 1993, concentrations of TCE in most monitoring wells have been declining gradually by natural attenuation.

In the Superfund area, TCE in ground water is present in surficial materials and fractured crystalline rock. The surficial materials consist mainly of glacially-derived sand and gravel overlain by a thick layer of glaciomarine clay in some areas (Lyford and others, 1999a). The marine clays are absent under the McKin site, but form a confining layer for ground water in buried coarse materials under part of the area between the site and the Royal River. In the area near Boiling Springs, the Royal River has eroded through the marine clays and exposed underlying coarse-grained materials. This area of exposed coarse-grained materials is the principal discharge area for the ground-water system to the north and west (fig. 14). Water samples from monitoring wells also indicate that the discharge of contaminants is focused in the area near Boiling Springs (Lyford and others, 1999a). Data from the monitoring wells also indicate that the TCE plume in fractured granite is coincident with the plume in overlying surficial materials. Samples were collected with PVD samplers during a period of low flow in the Royal River. Historical water-quality data indicate that concentrations of TCE in the river near the railroad trestle typically range from 15 to 20 µg/L for river discharges at the time of the study.

Purpose and Design of Sampling

The quantity of TCE that discharges to the Royal River, at river flows generally less than 100 ft^3/s, is great enough to cause concentrations in the river to exceed the State of Maine's water-quality standard for streams of 2.7 µg/L (P.R. Jaffe, Princeton University, written commun., 1996). In 1996, the Maine Department of Environmental Protection (MEDEP) and the USEPA sought, from the potentially responsible parties (PRPs) for the McKin site, an evaluation of remediation methods to reduce discharge of TCE into the river. The PRPs estimated that a 1,500-ft long interception system would be needed to successfully capture the TCE plume. Evaluation of remediation strategies and selection of a remediation program required an understanding of the configuration of the TCE plume near the river and the distribution of TCE concentrations across the width of the plume. Consequently, PVD samplers were installed along the Royal River and an unnamed tributary in the autumn of 1997 to determine the width of the TCE plume at the Royal River and variations in concentrations of TCE across the width of the plume (Lyford and others, 1999a) (fig. 15). In addition to these two goals, it was anticipated that results of the study would improve the understanding of contaminant pathways near the river.

Approximately 150 PVD samplers were placed along the banks of the Royal River and in several transects across the width of the river over a 3-day period in September 1997. Samplers also were placed along an unnamed tributary stream of the Royal River, in Boiling Springs, and in a seepage area on the north side of the river downstream from a river bend. After about 2 weeks, the samplers were retrieved and samples were analyzed on site with a portable gas chromatograph. The PVD samplers were retrieved at about the rate that they were analyzed in the field laboratory (about 50 per day). No samplers were lost during the study.

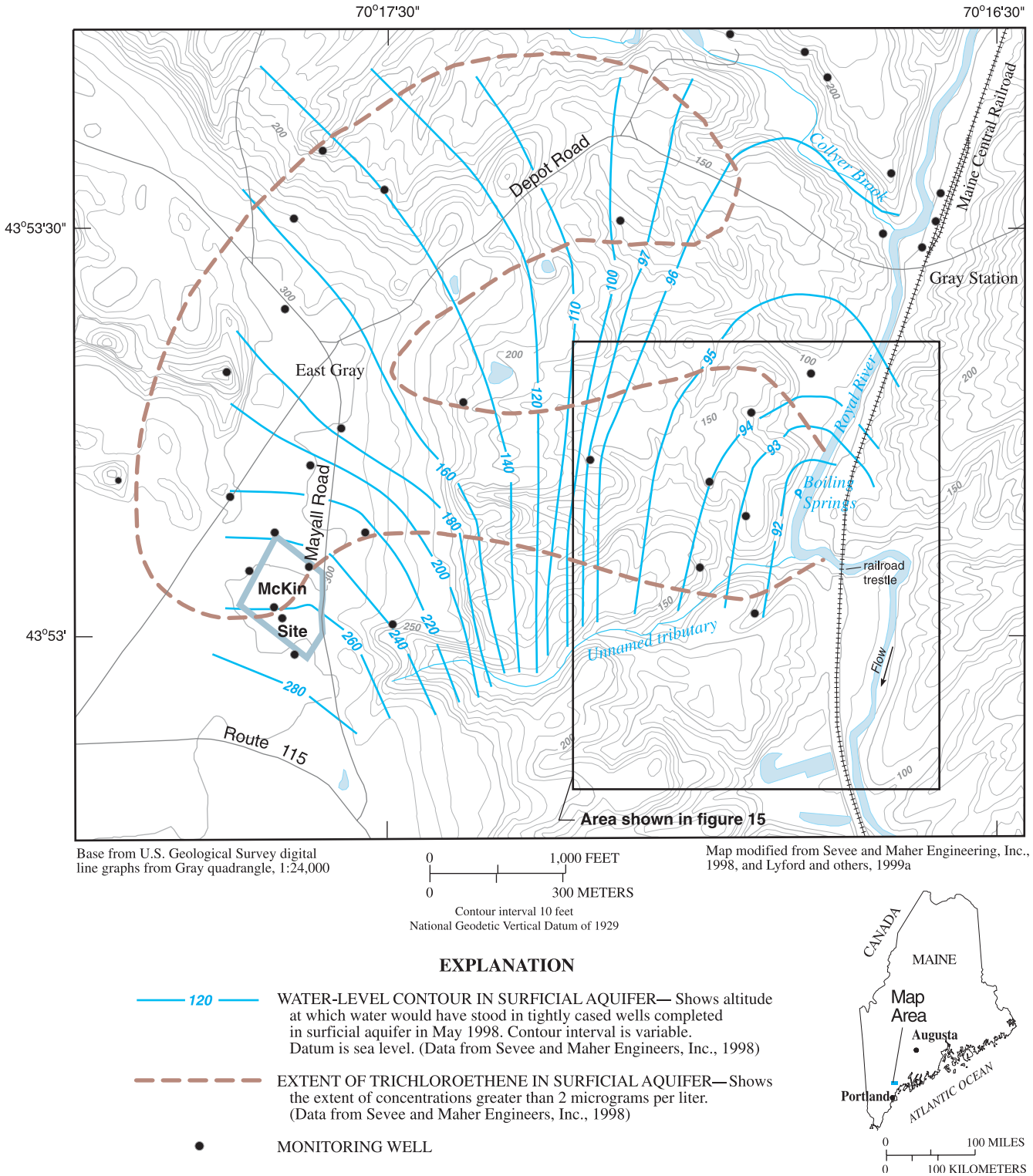
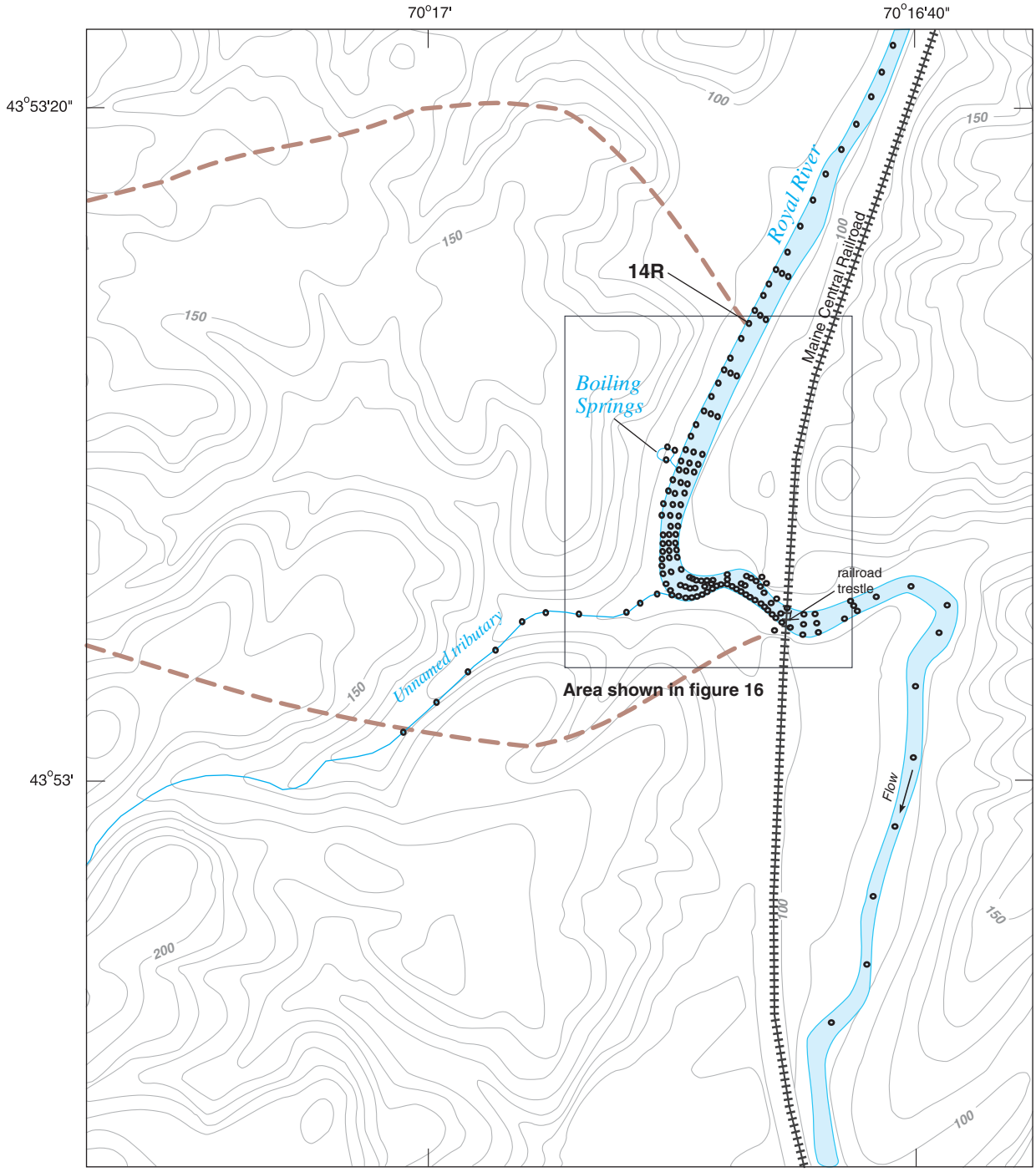


Figure 14. Location of the McKin Superfund Site and study area, potentiometric surface contours for the surficial aquifer, and extent of trichloroethene in ground water, Gray, Maine.



Base from U.S. Geological Survey digital line graphs from Gray quadrangle, 1:24,000

0 200 FEET
0 50 METERS

Map modified from Lyford and others, 1999a

CONTOUR INTERVAL 10 FEET
NATIONAL GEODETIC VERTICAL DATUM OF 1929

EXPLANATION

EXTENT OF TRICHLOROETHENE IN SURFICIAL AQUIFERÐShows the extent of concentrations greater than 2 micrograms per liter. (Data from Sevee and Maher Engineers, Inc., 1998)

PASSIVE-VAPOR-DIFFUSION SAMPLERS

Figure 15. Locations of passive-vapor-diffusion samplers installed in river-bottom sediment along and near the Royal River in September and October 1997, and extent of trichloroethene in ground water, Gray, Maine.

Results

The compound TCE was detected in most PVD samplers placed downstream of sampler 14R (fig. 16). The extent of the plume, as determined with PVD samplers, was generally consistent with plume maps drawn on the basis of water samples from wells (Sevee and Maher Engineers, Inc., 1998) (fig. 15). The highest concentrations, however, were focused in an area where sand boils were apparent in the riverbed a few hundred feet downstream from Boiling Springs, indicating a major discharge area for ground water and contaminants (fig. 16). In this general area, concentrations of TCE also were detected in samplers placed in the center of the river and on the opposite side, indicating that contaminated ground water was discharging across the width of the river and probably flowing beyond the river and floodplain downstream to points between the sharp easterly bend in the river and the railroad trestle (fig. 16). The VOCs detected downstream of the railroad trestle in an area outside of the mapped extent of the plume in ground water may result from the exchange of contaminated surface water with water in the bottom sediments. Hydraulic head data for the sediments and TCE concentrations for the river at the time of sampler retrieval would have been useful to test this possibility.

NUTMEG VALLEY ROAD SUPERFUND SITE, WOLCOTT AND WATERBURY, CONNECTICUT

By John R. Mullaney, Peter E. Church, *and* Carolyn J. Pina-Springer

Description of Study Area

Ground-water contamination by VOCs was discovered in the 1980s in the Nutmeg Valley area, Wolcott and Waterbury, Connecticut, and the area was classified by the USEPA as a Superfund site in 1989 (U.S. Environmental Protection Agency, 1989) (fig. 17), where approximately 43 industries and 25 residences use ground water, primarily from the bedrock aquifer, for industrial and domestic supply. Past disposal of industrial chemicals has been implicated in contamination of water from supply wells sampled by local, State, and Federal agencies during 1979–95. Contaminants may also be contributed to ground water from the City of Waterbury landfill (the North End Disposal Area), located about 1/2 mi upgradient from the Nutmeg Valley Road Superfund Site (fig. 17). The VOCs most commonly detected in supply wells tapping the crystalline-bedrock aquifer included TCE, PCE, and 1,1,1-trichloroethane (TCA). Concentrations of TCE were as high as 320 µg/L in samples collected from supply wells in 1985 (Mullaney and others, 1999).

Two principal aquifers underlie the Nutmeg Valley study area—an unconsolidated surficial aquifer consisting of glacial till, glacial stratified deposits, and postglacial alluvium, and a fractured crystalline bedrock aquifer consisting of well-foliated gneiss and granofels. Glacial till overlies the bedrock and is at land surface in most upland parts of the study area. Till is generally less than 10 ft thick; locally, however, it is more than 25 ft thick. Glacial derived stratified deposits in the valley, consisting of poor to well sorted layers of gravel, sand, silt and clay, range in thickness from 0 to 85 ft over till. A semi-confining layer of fine-grained deposits within the stratified deposits, 5 to 10 ft thick, overlies silty, sand and gravel in an area beneath the lower reaches of the unnamed tributary and Old Tannery Brook, and short reaches of the Mad River upstream and downstream of the confluence with Old Tannery Brook. Postglacial alluvial and swamp deposits are generally less than 10 ft thick and overlie glacial stratified deposits on the floodplain surfaces of the Mad River and Old Tannery Brook. These streams have incised deeply into glacial stratified deposits during postglacial time. The texture of the alluvium beneath the floodplain ranges widely from gravelly sand deposited in former stream-channel positions to fine sand and silt with significant amounts of organic material in overbank deposits laid down during floods (Mullaney and others, 1999).

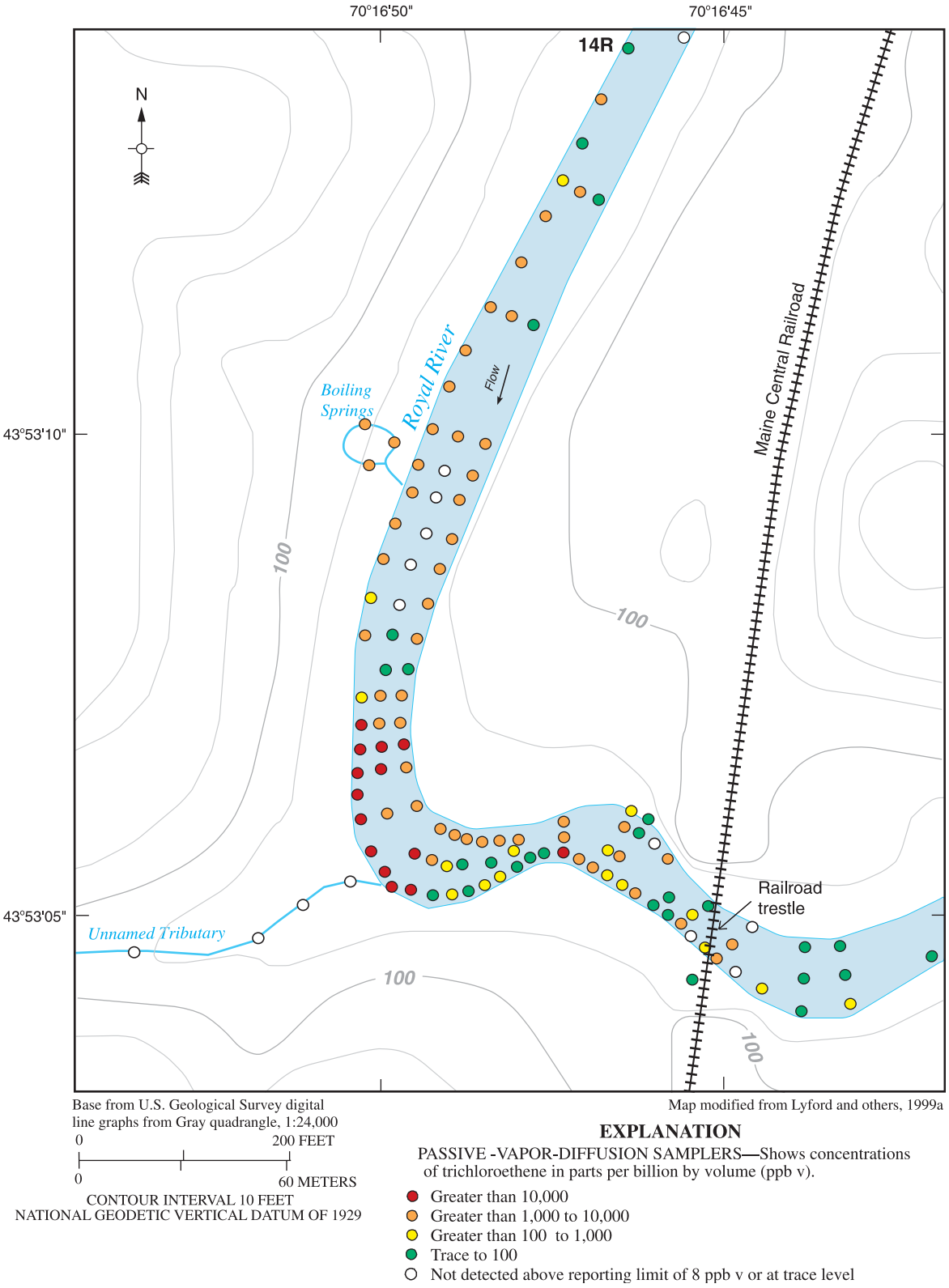
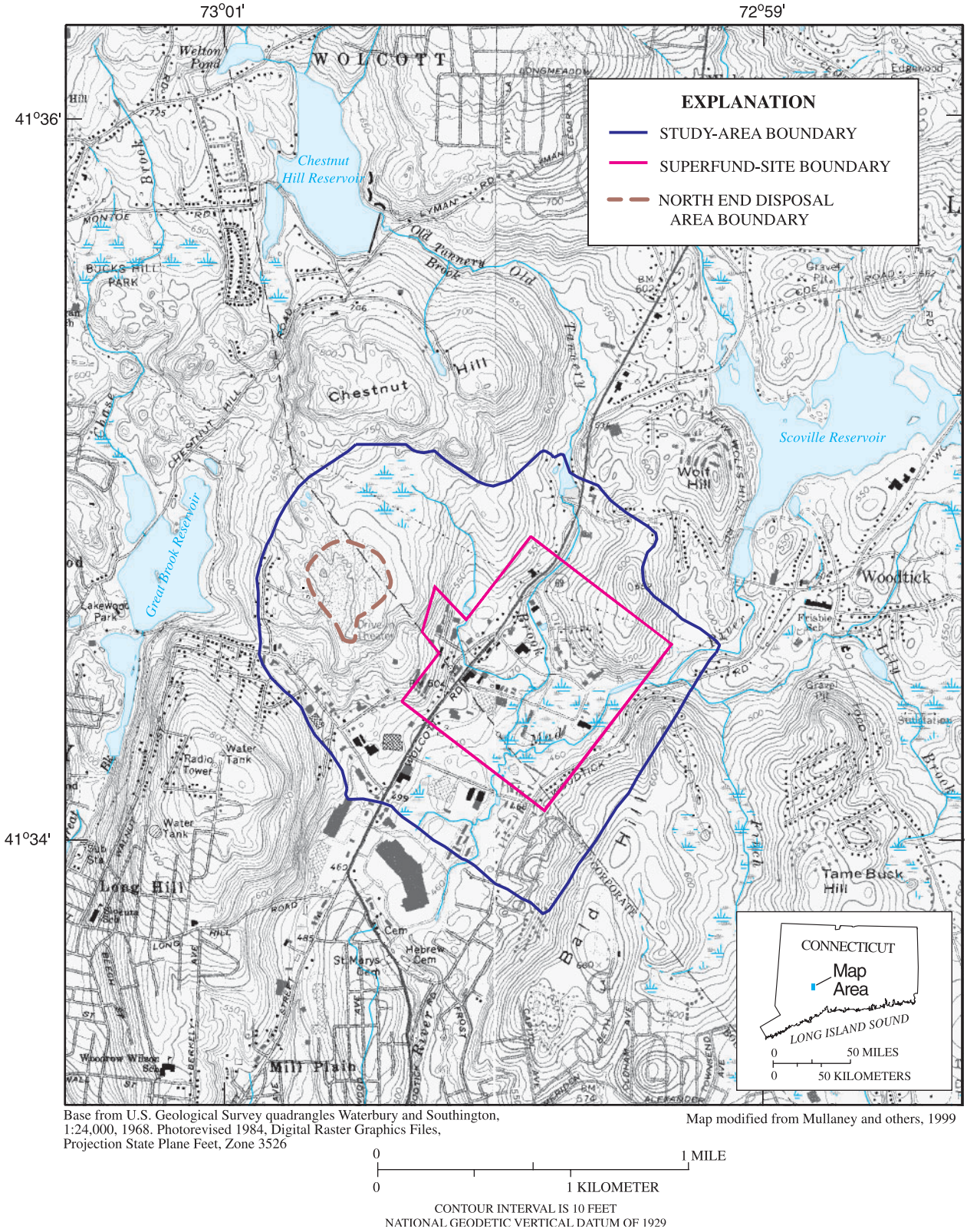


Figure 16. Concentrations of trichloroethene in passive-vapor-diffusion samplers installed in river-bottom sediments near Boiling Springs, Gray, Maine, September and October 1997.



Base from U.S. Geological Survey quadrangles Waterbury and Southington, 1:24,000, 1968. Photorevised 1984, Digital Raster Graphics Files, Projection State Plane Feet, Zone 3526

Map modified from Mullaney and others, 1999

0 1 MILE

0 1 KILOMETER

CONTOUR INTERVAL IS 10 FEET
NATIONAL GEODETIC VERTICAL DATUM OF 1929

Figure 17. Location of the Nutmeg Valley Road Superfund Site and study area, Nutmeg Valley, Wolcott and Waterbury, Connecticut.

Purpose and Design of Sampling

In 1997, the USGS, in cooperation with the Town of Wolcott and the USEPA, used PVD samplers as a reconnaissance tool for detecting and delineating ground-water discharge of VOCs into the local streams: Mad River, Old Tannery Brook, and an unnamed tributary to Old Tannery Brook (Mullaney and others, 1999). Samplers were installed in the river-bottom sediments at 154 sites along the Mad River, Old Tannery Brook, and an unnamed tributary of Old Tannery Brook on May 12-27, 1997, and were retrieved on July 8-10, 1997. Samplers were placed at 100- to 200-ft intervals in the center of the streams and in transects across the stream at selected locations (fig. 18). Because the PVD-sampler technology was new, a second round of sampling was done for comparison with results obtained from the first round of sampling. On October 23-28, 1997, 128 PVD samplers were installed at locations similar to those in the first sampling round. These samplers were retrieved on November 11-13, 1997 (fig. 19). The USEPA analyzed both sets of samples on site with a gas chromatograph calibrated for measurement and identification of TCE, PCE, and petroleum compounds (Mullaney and others, 1999). In addition, vertical head gradients between the ground water and surface water were measured in November 1997 at 30 locations along Old Tannery Brook, the unnamed tributary to Old Tannery Brook, and the Mad River to determine if and where ground water was discharging to the streams.

Results

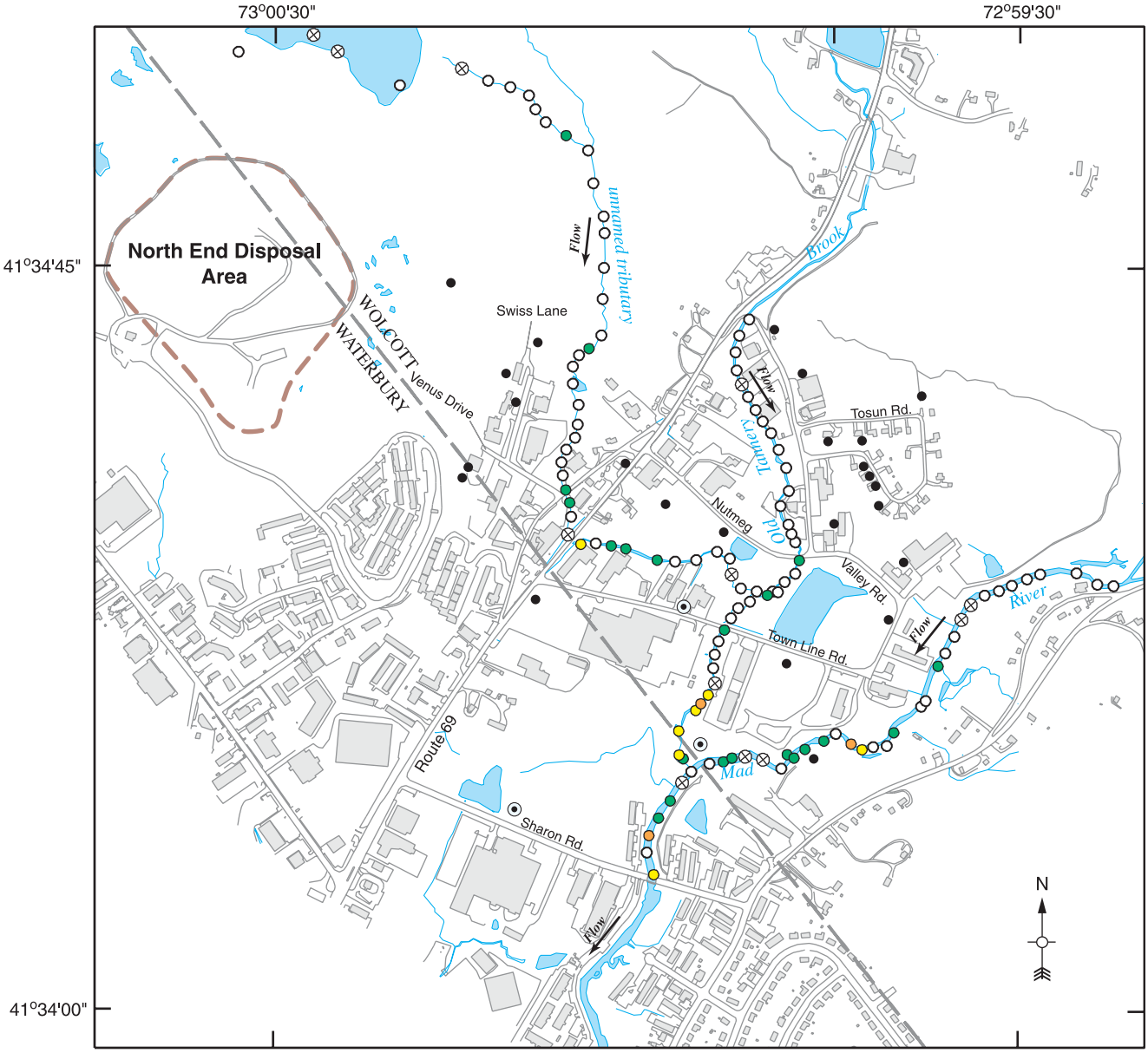
Results from the first round of sampling show that the highest concentrations and most frequent detections of VOCs were in zones along the lower reach of Old Tannery Brook and in the Mad River at short distances upstream and downstream from the confluence with Old Tannery Brook (fig. 18). Concentrations of TCE ranged from not detected (less than 5 ppb v) to 4,800 ppb v. Concentrations of PCE ranged from not detected (less than 5 ppb v) to 781 ppb v. Adhesive tape used to secure the samplers to the surveyor flags in the first round of sampling was found to contain petroleum compounds; therefore, detections of these compounds in PVD samples were not reported.

The second round of samplers were retrieved in November 1997 to determine if the July 1997 results were reproducible. Instead of tape, nylon ties were used to secure surveyor flags to the samplers, to avoid problems with contamination by petroleum compounds. The spatial pattern of VOCs detected was similar to the July 1997 detection pattern (fig. 19), but with fewer detections of PCE and with additional locations where trace-levels of *cis*-DCE were detected. This difference was due to a small difference in the calibration of the gas chromatograph between the two sampling rounds. Concentrations of TCE in vapor ranged from not detected (less than 25 ppb v) to greater than 30,000 ppb v. Concentrations of PCE ranged from not detected (less than 25 ppb v) to 390 ppb v. Concentrations of benzene ranged from not detected (less than 25 ppb v) to 51 ppb v.

In both sampling rounds, the highest vapor concentrations were detected along the lower reach of Old Tannery Brook near a known contaminated area on the western side of the brook that contains primarily TCE, PCE, vinyl chloride, and *cis*-DCE in soils and ground water (Loureiro Engineering Associates, 1998a, b). Ground-water contaminated by TCE also has been documented on the eastern side of Old Tannery Brook (HRP Associates, 1991). This area is underlain by the fine-grained deposits (semi-confining lacustrine deposit), which suggests that VOCs discharged to the brook are from contaminated ground water in the post-glacial alluvium. The high vapor concentrations of TCE detected along the Mad River may be from ground-water-contaminant plumes in surficial deposits beneath the fine-grained layer, or from the fractured bedrock, or both.

In both sampling rounds, vapor concentrations of TCE and PCE were detected in the unnamed tributary, but were lower than those detected in the Old Tannery Brook and the Mad River (figs. 18 and 19). In the first sampling round, the highest TCE and PCE vapor concentrations were detected 1,200 ft upstream of the Old Tannery Brook; concentration of TCE was 73 ppb v, and PCE was 348 ppb v. The highest vapor concentrations in the second sampling round were detected 1,600 ft upstream of Old Tannery Brook; concentration of TCE was 104 ppb v and PCE was 101 ppb v.

Variations in vapor concentrations across stream channels were observed at sites where PVD samplers were installed at the edges and in the center of the channel. These variations are probably due to the direction from which the VOCs originate, and also may be caused by variations in organic matter, biotic and abiotic processes, and streambed-hydraulic conductivity.



Base from U.S. Army Corps of Engineers, 1993, 1997, Scale 1:2,400
Projection: State Plane Feet, Zone 3526

0 1,000 FEET
0 300 METERS

Map modified from Mullaney and others, 1999

EXPLANATION

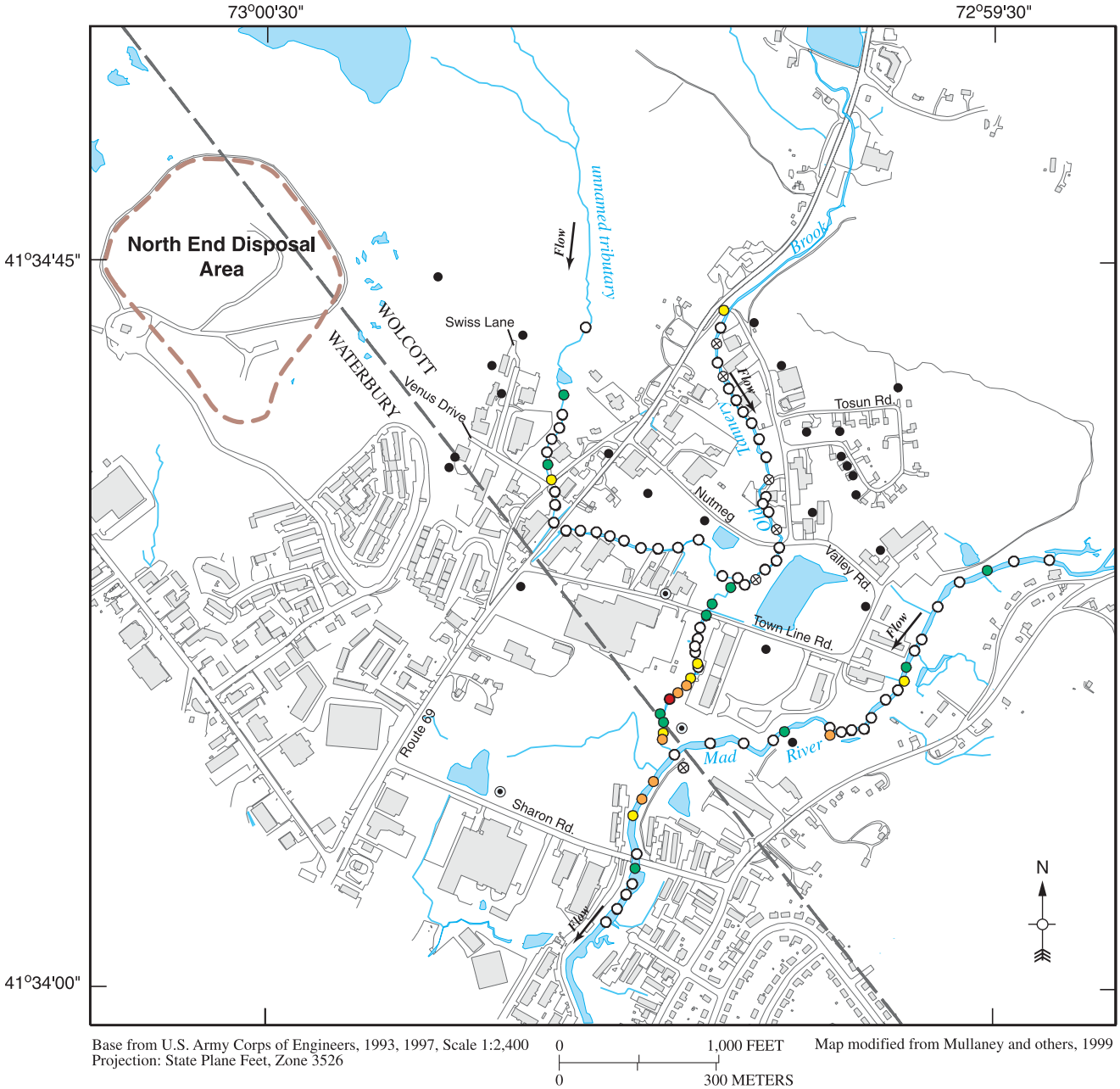
PASSIVE-VAPOR-DIFFUSION SAMPLERS—Shows concentrations of trichloroethene and tetrachloroethene in parts per billion by volume (ppb v), July 1997.

- Greater than 1,000 to 10,000
- Greater than 100 to 1,000
- Trace to 100
- Not detected above reporting limit of 5 ppb v or at trace level
- Sampler not found

MONITORING WELLS—Shows concentrations of trichloroethene and tetrachloroethene in ground water in micrograms per liter (µg/L). Wells sampled May to September, 1998 (Mullaney and others, 1999)

- Trace to 100 µg/L
- Not detected above reporting limit of 1 µg/L or at trace level

Figure 18. Concentrations of trichloroethene plus tetrachloroethene in passive-vapor-diffusion samplers installed in river-bottom sediments of the Mad River, Old Tannery Brook, and an unnamed stream, Nutmeg Valley, Wolcott and Waterbury, Connecticut, July 1997.



EXPLANATION

PASSIVE-VAPOR-DIFFUSION SAMPLERS—Shows concentrations of trichloroethene and tetrachloroethene in parts per billion by volume (ppb v), November 1997.

- Greater than 10,000
- Greater than 1,000 to 10,000
- Greater than 100 to 1,000
- Trace to 100
- Not detected above reporting limit of 25 ppb v or at trace level
- Sampler not found

MONITORING WELLS—Shows concentrations of trichloroethene and tetrachloroethene in ground water in micrograms per liter (µg/L). Wells sampled May to September 1998 (Mullaney and others, 1999)

- Trace to 100 µg/L
- Not detected above reporting limit of 1 µg/L or at trace level

Figure 19. Concentrations of trichloroethene plus tetrachloroethene in passive-vapor-diffusion samplers installed in river-bottom sediments of the Mad River, Old Tannery Brook, and an unnamed stream, Nutmeg Valley, Wolcott and Waterbury, Connecticut, November 1997.

BAIRD & McGUIRE SUPERFUND SITE, HOLBROOK, MASSACHUSETTS

By Jennifer G. Savoie and Melissa G. Taylor

Description of Study Area

A ground-water plume containing volatile and semi-volatile organic compounds at the Baird & McGuire Superfund Site in Holbrook, Massachusetts, extends eastward from a former chemical-processing plant toward and beneath the Cochato River (fig. 20) (M.G. Taylor, Environmental Protection Agency, written commun., 1998). The Cochato River once supplied water to the towns of Holbrook, Randolph, and Braintree, but use of this source ended after contamination near the river was discovered in 1983. In 1993, a ground-water-extraction system began operation to remove contaminants from a sand and gravel aquifer below the site and the river and to limit the discharge of contaminants to the river. From 1995 to 1997, contaminated sediments were excavated from the river and incinerated as part of site remediation. Despite these remedial actions, the USEPA and residents are concerned that contaminants from the ground-water plume could discharge to the river (Savoie and others, 1999).

Purpose and Design of Sampling

In March and April 1998, a network of PVD samplers was installed along the Cochato River to determine if VOC-contaminated ground water was discharging through the river-bottom sediments while a ground-water-extraction system was operating and after the system had been shut down for 2 weeks (fig. 21). Drive-point piezometers were installed at four locations within the riverbed of the Cochato River near the known extent of the ground-water plume. Water levels from piezometers were compared to river-stage measurements to determine if the river was gaining ground water across the study area and if contaminants could potentially discharge into the river (Savoie and others, 1999).

Results

Under pumping and non-pumping conditions, petroleum compounds (benzene, ethylbenzene, *meta/para*-xylene, *ortho*-xylene, and toluene) were detected in PVD samplers where the plume passes beneath the river (fig. 21, showing concentrations under pumping conditions). Concentrations of total petroleum compounds ranged from not detected upriver of plume area, but downriver adjacent to the plume area concentrations were greater than 200,000 ppb v. Under pumping and non-pumping conditions, concentrations did not differ significantly. The compounds TCE, PCE, and *cis*-DCE also were detected in PVD samplers more than 200 ft downstream of the area where the petroleum compounds were detected. These detections indicate a different source for TCE + PCE than for the petroleum compounds (fig. 21).

Water levels in four piezometers were consistently higher than the river stage, which indicates an upward hydraulic gradient and ground-water discharge to the river. This observation in the piezometers and the presence of contaminants in the pore water of river-bottom sediments indicate that contaminants from the Baird & McGuire Superfund Site ground-water plume were discharging into the Cochato River at the time of this study for both pumping and non-pumping conditions.

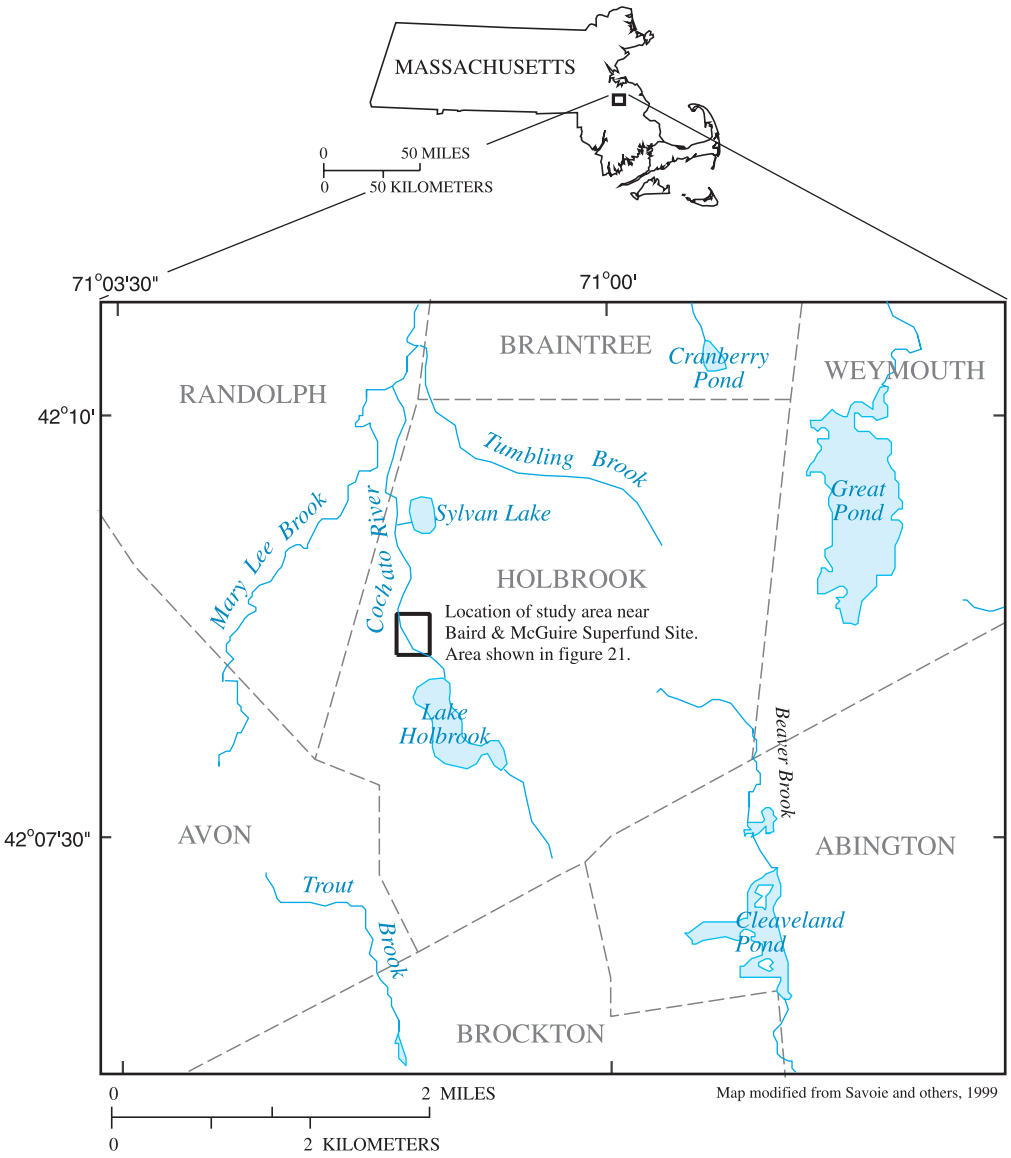


Figure 20. Location of the Baird & McGuire Superfund Site and study area, Holbrook, Massachusetts.

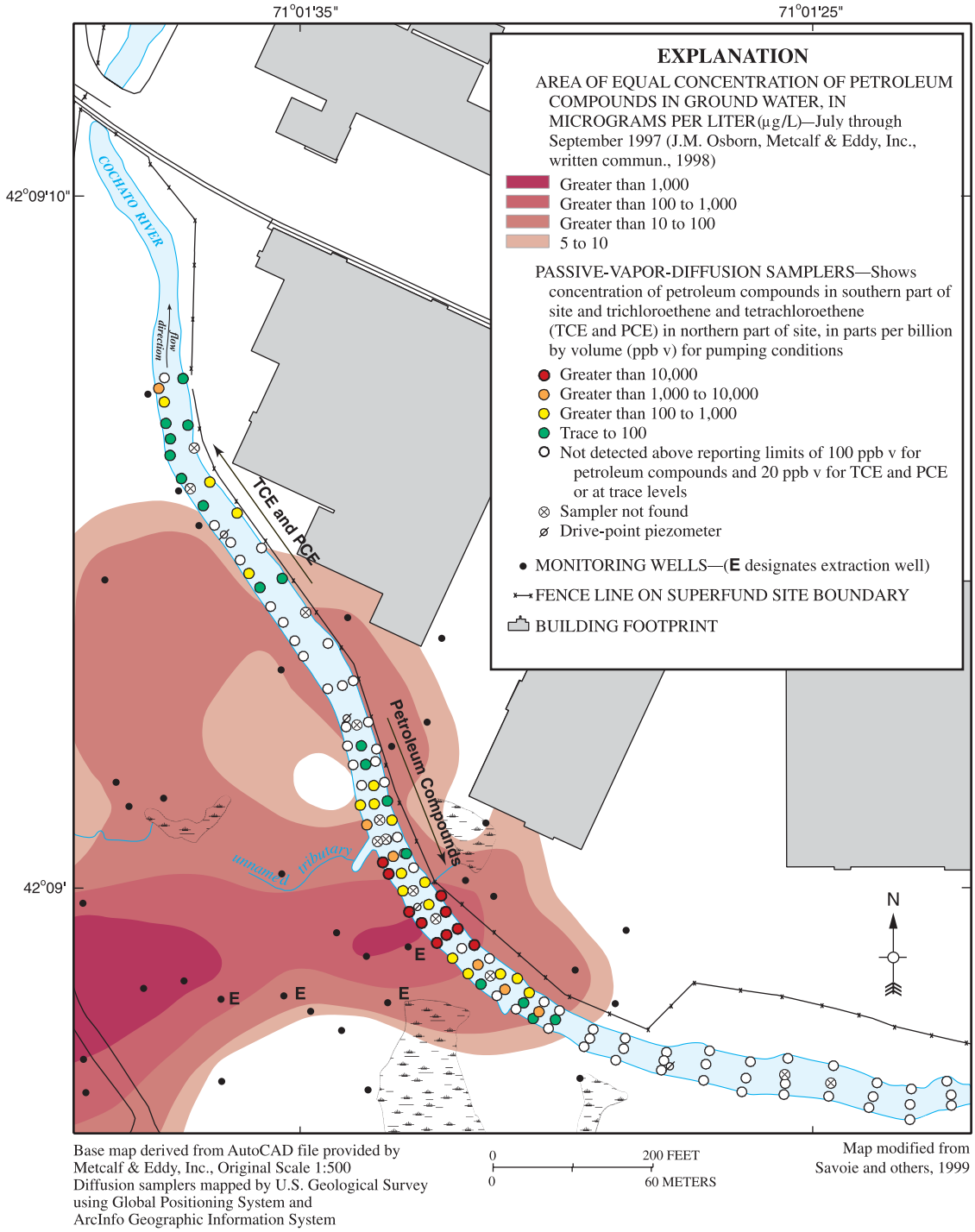


Figure 21. Concentrations of trichloroethene plus tetrachloroethene and petroleum compounds in passive-vapor-diffusion samplers installed in river-bottom sediments of the Cochato River, Baird & McGuire Superfund Site, Holbrook, Massachusetts, March and April 1998.

ALLEN HARBOR LANDFILL, DAVISVILLE NAVAL CONSTRUCTION BATTALION CENTER SUPERFUND SITE, NORTH KINGSTOWN, RHODE ISLAND

By Forest P. Lyford, William C. Brandon, *and* Christine A.P. Williams

Description of Study Area

The Allen Harbor Landfill at the former Davisville Naval Construction Battalion Center in North Kingstown, Rhode Island (fig. 22), was used by the U.S. Navy from 1946 until 1974 to dispose of wastes, including municipal-type waste, construction debris, paint thinners, degreasers, sewerage sludge, and fuel oil (EA Engineering, Science, and Technology, 1996). This approximately 15-acre landfill on the west side of Allen Harbor is bordered on the west by Sanford Road and a large wetland, and is bordered on the north and south by small vegetated wetlands (fig. 23).

Landfill wastes are up to 20 ft thick. Geologic materials beneath landfill wastes and the shoreline include a discontinuous layer of fine to very fine sand, generally less than 15 ft thick, over a layer of silt that is 20 to 50 ft thick. Peat layers are in some locations at the top of the sand layer. The silt layer overlies a discontinuous till layer or bedrock. The altitude of the bottom of the silt layer ranges from 30 to 50 ft below sea level (EA Engineering, Science, and Technology, 1996). Monitoring wells, some in clusters, are completed in the upper sand layer (S following the well number indicates a shallow screen depth), the silt layer (I following the well number indicates a intermediate screen depth), and till (D following the well number indicates a deep screen depth) (fig. 23).

Shallow ground water in landfill wastes and the upper sand layer flows eastward from a water-table mound centered near well MW09-18I (fig. 23) to the shore and southward toward a mudflat area. During the wet season, shallow ground water also flows westward toward a wetland on the west side of Sanford Road. The mound is not apparent in water levels from wells screened at greater depths near and below the bottom of the silt layer. Ground-water flow at depth is predominantly eastward and southeastward toward Allen Harbor (fig. 23). Vertical hydraulic gradients are downward in the area of the water-table mound and upward near the shore. Gradients reverse in some wells near the shore during high tide, but this reversal has not been consistently observed for all tidal cycles (EA Engineering, Science, and Technology, 1996).

A variety of VOCs, including petroleum and chlorinated compounds have been detected in samples from several monitoring wells within the landfill area (fig. 23) (EA Engineering, Science, and Technology, 1996). Concentrations of VOCs also have been detected in water from borings installed in sediments offshore in the harbor (EA Engineering, Science, and Technology, 1998a).

Purpose and Design of Sampling

The high concentrations of VOCs in samples from monitoring wells prompted the use of PVD samplers to identify potential discharges of VOC-contaminated ground water along the shore. Because PVD samplers had not been used previously in a coastal setting, a secondary goal of this study and a companion study in nearby Calf Pasture Point (fig. 22) was to determine if PVD samplers can yield useful information about discharge points of VOCs along a tidally affected shoreline (Lyford and others, 1999b).

The PVD samplers were installed during March 16 through 20, 1998, at locations shown in figure 23 and retrieved on April 1 through 2, 1998. Most samplers (79) were installed during low tide at intervals of about 25 ft along about 1,700 ft of shoreline. Samplers also were placed at the high-tide level at 20 locations for comparison to results from low-tide locations, in 12 seeps where ground water was apparently discharging near the base of the landfill, and at 4 locations on mudflats south of the landfill.

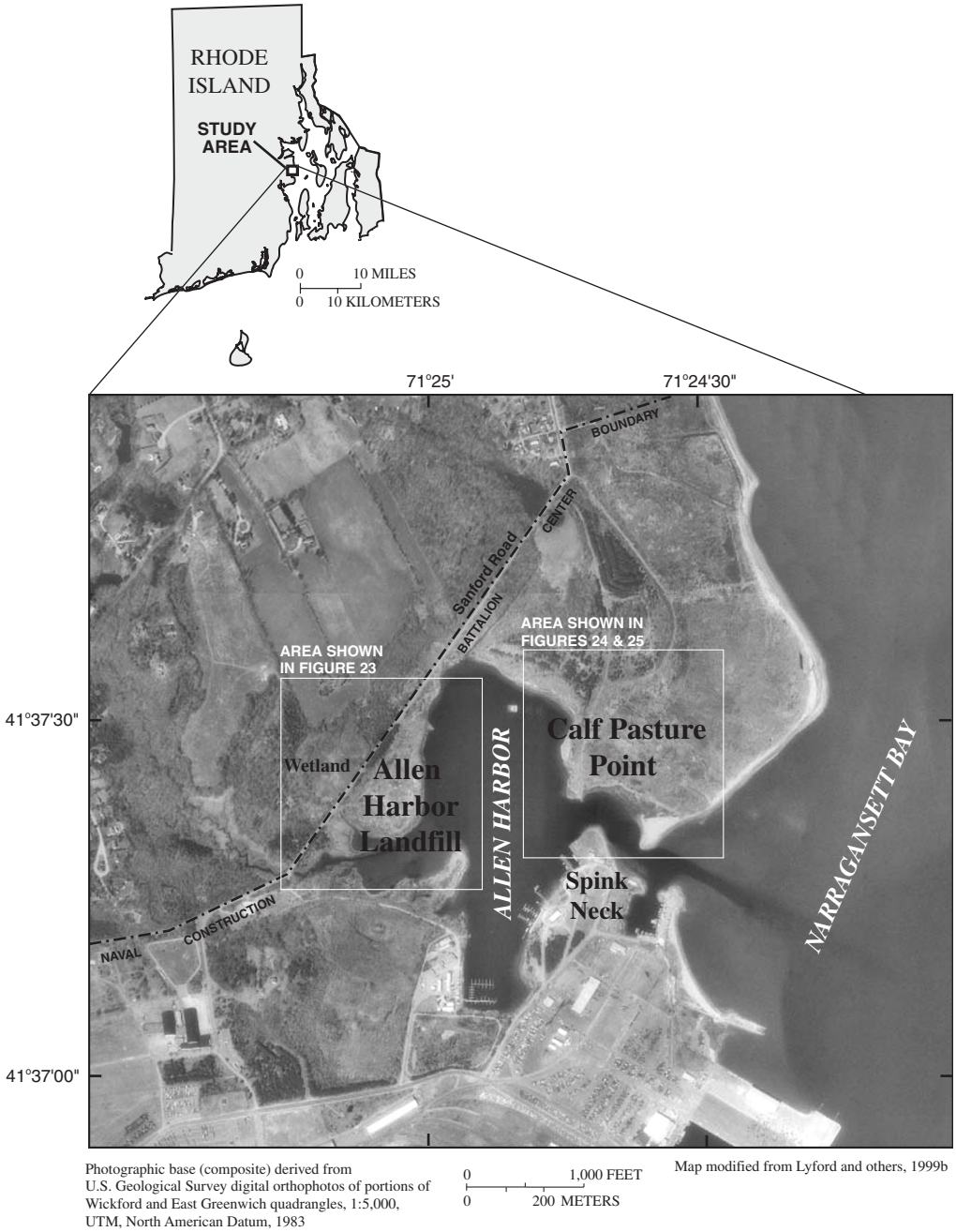
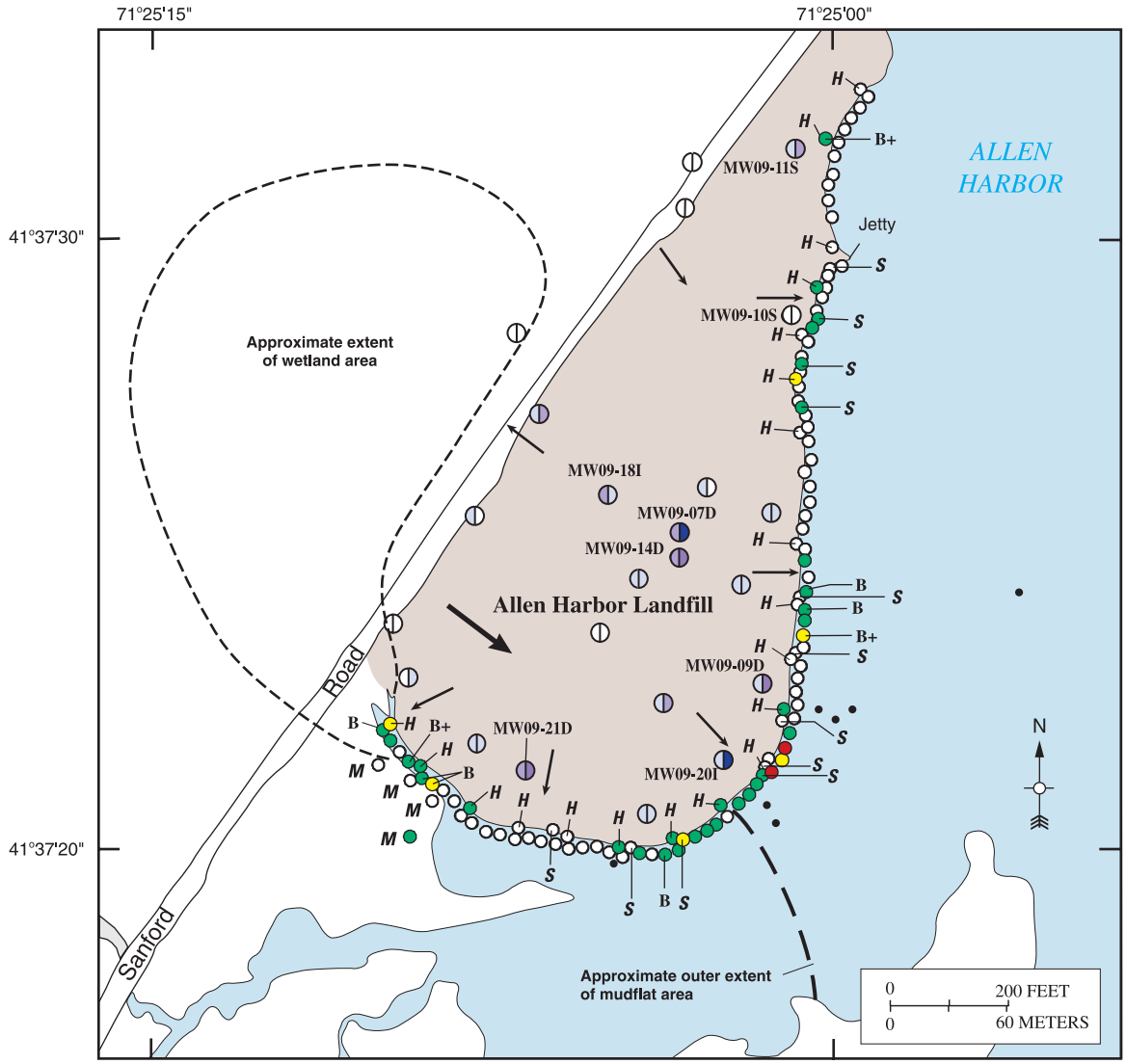


Figure 22. Locations of the Allen Harbor Landfill and Calf Pasture Point study areas, Davisville Naval Construction Battalion Center Superfund Site, North Kingstown, Rhode Island.



Base traced from U.S. Geological Survey digital orthophoto, 1:12,000, GPS from Trimble Asset Surveyor, 1927 North American Datum.

Map modified from Lyford and others, 1999b

EXPLANATION

APPROXIMATE EXTENT OF LANDFILL

PASSIVE-VAPOR-DIFFUSION SAMPLERS INSTALLED IN LOW-TIDE ZONE OR HIGH-TIDE ZONE (***H***), NEAR SEEP (***S***), OR ON MUDFLAT (***M***)—Shows concentrations of trichloroethene (TCE) and tetrachloroethene (PCE) in parts per billion by volume (ppb v); **B**, if only benzene is detected; **B+**, if benzene is detected with TCE and PCE.

- Greater than 10,000
- Greater than 1,000 to 10,000
- Greater than 100 to 1,000
- Trace to 100
- Not detected above reporting limits of 20 ppb v for TCE and PCE and 10 ppb v for Benzene or a trace levels

MW09-20I SELECTED MONITORING WELL AND NUMBER IF INDICATED—Shows concentrations of (left side) petroleum compounds and (right side) chlorinated compounds at single well or highest concentration at well cluster, in micrograms per liter (µg/L). Wells sampled in May 1995 (EA Engineering, Science, and Technology, 1996)

- Greater than 10,000
- Greater than 1,000 to 10,000
- Greater than 100 to 1,000
- Trace to 100
- Not detected above or below detection limit

OFFSHORE BORINGS—Volatile organic compounds detected in water from offshore borings (EA Engineering, Science, and Technology, 1998b)

GENERALIZED DIRECTION OF SHALLOW GROUND-WATER FLOW IN UPPER SAND UNIT

GENERALIZED DIRECTION OF DEEP GROUND-WATER FLOW

Figure 23. Directions of ground-water flow in the shallow and deep surficial aquifers, concentrations of volatile organic compounds in ground water beneath the Allen Harbor Landfill, December 1995, and concentration of trichloroethene in passive-vapor-diffusion samplers installed in tidal-zone sediments along the shoreline of Allen Harbor Landfill, April 1998, Davisville Naval Construction Battalion Center Superfund Site, North Kingstown, Rhode Island.

Results

Concentrations of VOCs were detected in 41 of 115 vapor samplers placed near the Allen Harbor Landfill. The most common VOC detected in the samplers was TCE. Other VOCs detected included benzene, toluene, and PCE. Vapor concentrations for total VOCs exceeded 100 ppb v at eight locations (fig. 23). VOCs were detected at 10 of the 20 high-tide locations and at 5 of the 12 seeps. Comparison of the sample results at the 20 locations where high-tide and low-tide samplers were installed shows that where VOCs were detected in the 10 high-tide samples, VOCs were detected in only 3 of the companion low-tide samples; and where VOCs were not detected in the remaining 10 high-tide samples, VOCs were detected in 2 of the low-tide samples. The concentrations detected at seeps were generally near minimum reporting levels, indicating that the seeps were not major discharge areas for VOCs. A trace of TCE was detected at one mudflat location.

Highest VOC detections were in samplers that were placed near well MW09-20I, where high VOC concentrations were detected in ground water. The extent of the area where VOCs were detected near well MW09-20I indicates a VOC plume in ground water under the landfill that is at least 300 ft wide at the shore. The extent of the plume near well MW09-20I had not been mapped previously.

CALF PASTURE POINT, DAVISVILLE NAVAL CONSTRUCTION BATTALION CENTER SUPERFUND SITE, NORTH KINGSTOWN, RHODE ISLAND

By Forest P. Lyford, Christine A.P. Williams, *and* William C. Brandon

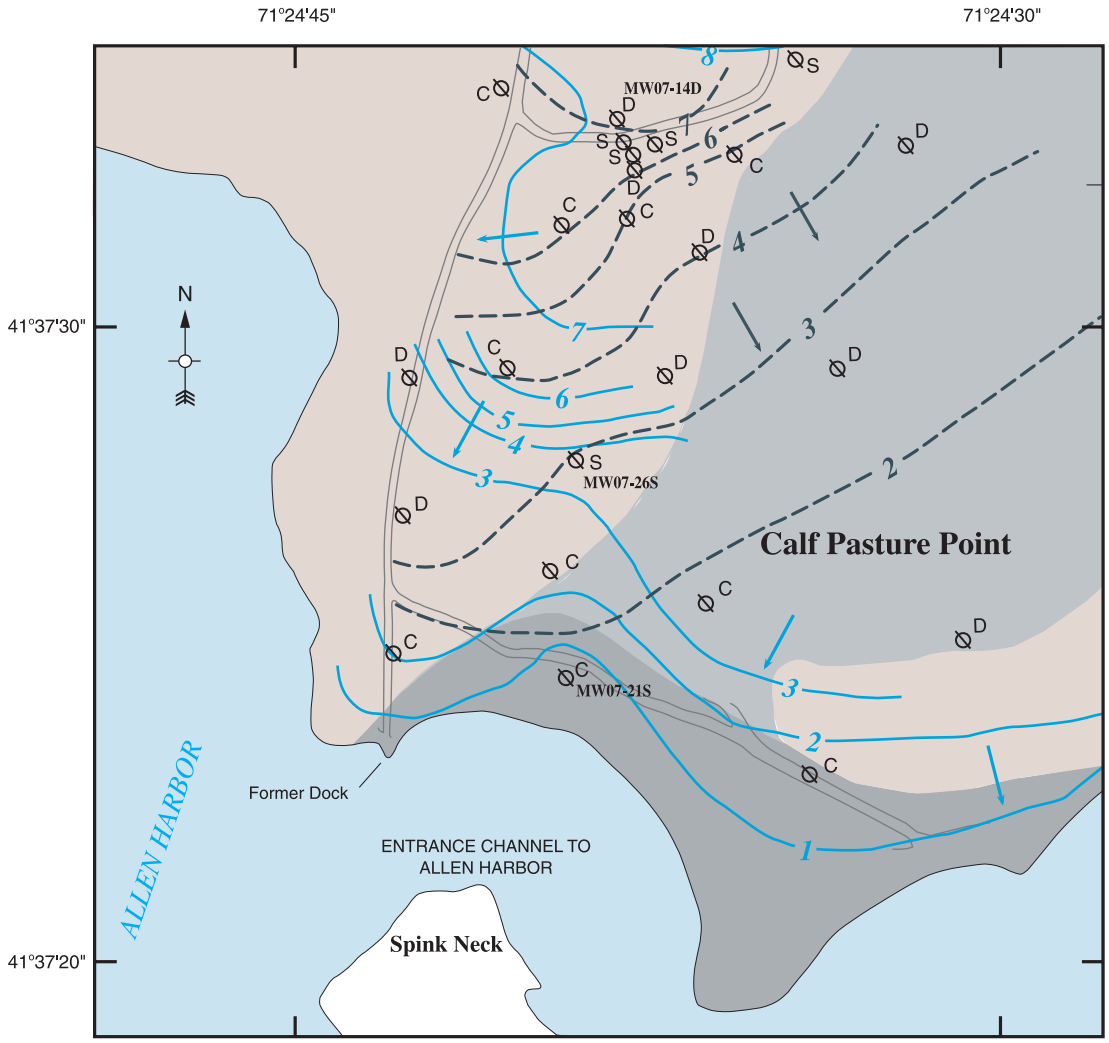
Description of Study Area

Calf Pasture Point is an area between Allen Harbor and Narragansett Bay in North Kingstown, Rhode Island (fig. 22), and was part of the former Davisville Naval Construction Battalion Center. Former waste-disposal activities in the area caused contamination of ground water by VOCs (EA Engineering, Science, and Technology, 1998b).

The land-surface altitude in the area shown in figure 24 ranges from about 14 ft above sea level near well MW07-14D to sea level at the shore line. Depth to fractured crystalline bedrock ranges from near land surface near monitoring well MW07-14D (fig. 24) to a maximum depth of about 70 ft near Narragansett Bay at the southeastern corner of figure 24. Bedrock depths are about 30 to 40 ft near the shore of Allen Harbor and at the entrance channel to Allen Harbor. An upper sand layer consisting of fine to very fine sand overlies a layer of silt, which, in turn, overlies till or bedrock. The silt layer is absent along a north-south-trending till ridge between wells MW07-26S and MW07-21S, where the upper sand overlies till. The upper sand layer includes materials that were dredged from the harbor or bay and placed in a former lagoon in the central part of the study area and also consists of materials formed by recent sedimentation on the southern end of the study area (fig. 24) (Church and Brandon, 1999).

Ground water in the upper sand layer flows semi-radially outward from a topographic high area near well MW07-14D toward Narragansett Bay, Allen Harbor, and the entrance channel to Allen Harbor. Ground-water-flow direction is generally to the southeast in the deep till aquifer (fig. 24) (Church and Brandon, 1999). Vertical hydraulic gradients generally are downward, but near well MW07-21S upward gradients have been observed, except during high tide when the gradient is zero or downward (EA Engineering, Science, and Technology, 1997). Conceptually, shallow ground water discharges within the intertidal zone or at shallow depths beyond the intertidal zone, and deep ground water in till and bedrock discharges in the intertidal zone or further offshore. Data, however, are not available for confirmation of discharge points. Shallow ground water also appears to discharge to small wetland areas near the entrance channel to Allen Harbor (fig. 25).

A plume of VOCs in ground water extends from the general area of monitoring well MW07-14D towards Narragansett Bay, the entrance channel to Allen Harbor, and Allen Harbor (fig. 25). The VOCs detected in the plume include vinyl chloride, 1,2-dichloroethene, PCE, TCE, and 1,1,2,2-tetrachloroethane. Consequently, highest concentrations of VOCs in ground water are in wells completed below the silt layer at depths of 30 ft or more in till and bedrock. In the area of the till ridge where the silt layer is absent, VOCs are at shallow depths of 25 ft or less (EA Engineering, Science, and Technology, 1998b).



EXPLANATION

WATER-LEVEL CONTOUR IN UPPER SAND AND LOWER TILL—Shows altitudes at which water would have stood in tightly cased wells completed in the upper sand and the deep till deposits, December 1, 1995. Contour interval is 1 foot.

1 — Shallow wells in sand

2 — Deep wells in till

GENERALIZED GROUND-WATER FLOW DIRECTION IN UPPER SAND

GENERALIZED GROUND-WATER FLOW DIRECTION IN LOWER TILL

APPROXIMATE LAND-SURFACE CONFIGURATION OF CALF PASTURE POINT BEFORE FILLING WITH DREDGED MATERIAL

APPROXIMATE EXTENT OF DREDGED FILL AND FORMER LAGOON

POST-1966 SEDIMENTATION

MW07-21S WELL SITES, NUMBER, AND SAMPLING DEPTHS

S Shallow (sand)

D Deep (till)

C Cluster (shallow and deep)

Figure 24. Potentiometric surfaces and generalized ground-water-flow directions for the shallow and deep surficial aquifers, Calf Pasture Point, Davisville Naval Construction Battalion Center Superfund Site, North Kingstown, Rhode Island, December 1995.

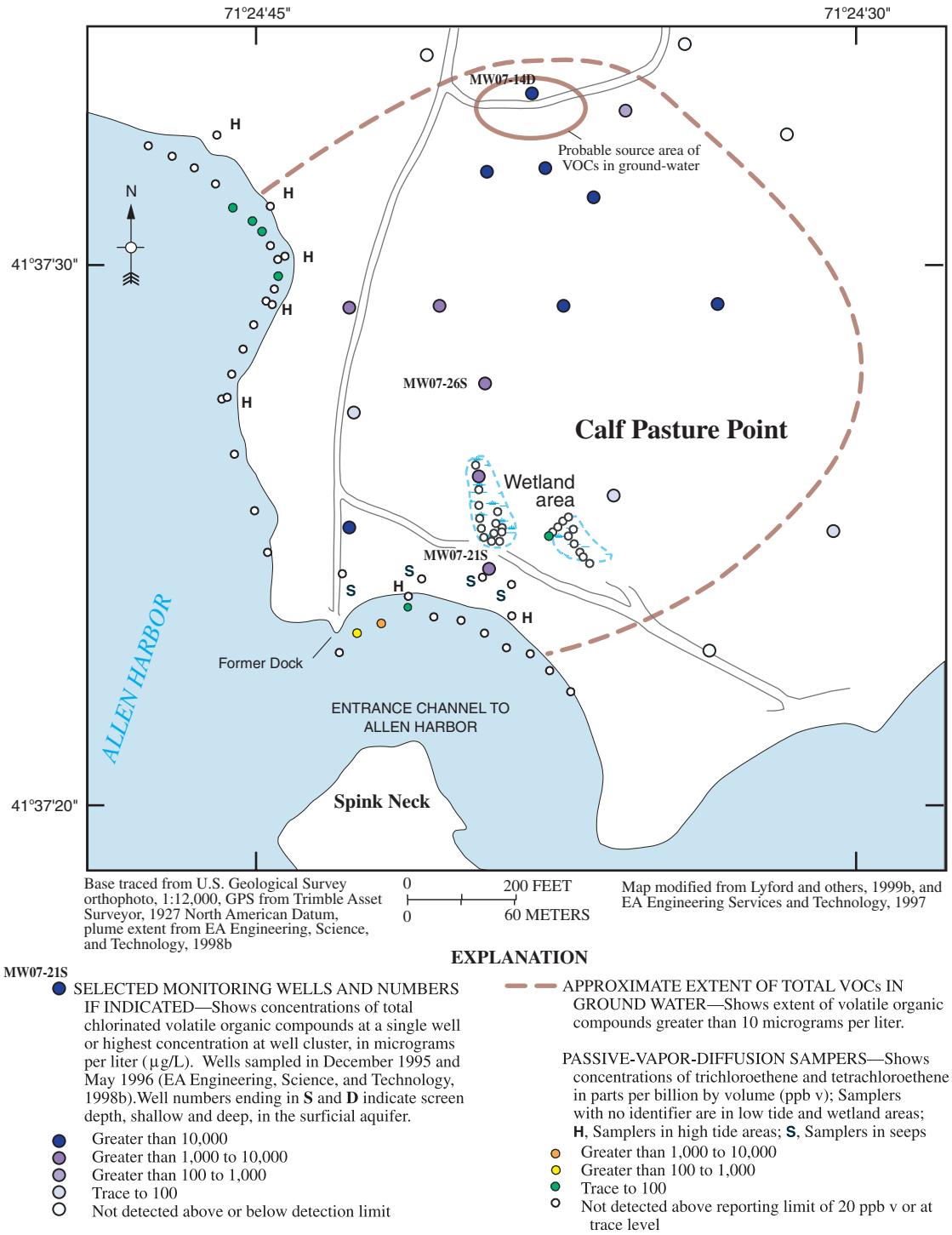


Figure 25. Concentrations of trichloroethene in passive-vapor-diffusion samplers installed in the tidal-zone sediments along the shoreline and in wetland-bottom sediments near the shoreline, Calf Pasture Point, Davisville Naval Construction Battalion Center Superfund Site, North Kingstown, Rhode Island, March and April 1998.

Purpose and Design of Sampling

The PVD samplers were used at Calf Pasture Point to identify possible discharge areas of VOC-contaminated ground water. Other than the study at the nearby Allen Harbor Landfill, PVD samplers had not been used previously in a coastal setting. Consequently, a secondary goal of the study was to determine if PVD samplers can yield useful information about areas of VOC discharge along a tidally affected shoreline (Lyford and others, 1999b).

The PVD samplers were installed along the shoreline in the area of the VOC plume at low- and high-tide locations, in two wetland areas inland from the entrance channel to Allen Harbor, and in four seeps in or near the intertidal zone. The samplers were installed during April 7 through 9, 1998, at 65 locations (fig. 25), and retrieved during April 28 through 29, 1998. The shoreline shown on figure 25 is approximately the extent of water at high tide. Most samplers were placed during low tide at intervals of 50 ft along about 1,500 ft of shoreline. Because of the limited number of samplers available at the time of the study, the southwestern side of the study area was given a lower priority, and the distances between samplers was greater than elsewhere. Samplers were placed at the high-tide level at seven locations for comparison to results from low-tide locations.

Results

Concentrations of VOCs were detected in samples from 7 of 37 PVD samplers placed within the intertidal zone at Calf Pasture Point and in samples from 1 of 24 samplers placed in wetland areas. Concentrations of VOCs were not detected in seepage areas. The compound TCE was the only VOC detected, except for a trace of PCE detected in one sample (Lyford and others, 1999b). Concentrations of TCE detected in the PVD samplers ranged from a trace to 1,900 ppb v (fig. 25). The occurrences of VOCs along the shoreline were later confirmed by sampling from drive-point wells.

OTIS AIR NATIONAL GUARD/CAMP EDWARDS SUPERFUND SITE, JOHNS POND, FALMOUTH, MASSACHUSETTS

By Jennifer G. Savoie *and* Denis R. LeBlanc

Description of Study Area

A plume of dissolved VOCs in ground water extends 9,000 ft from the site of a storm drain on the Otis Air National Guard/Camp Edwards Superfund Site, also known as the Massachusetts Military Reservation (MMR), to Johns Pond, Mashpee, in the Cape Cod area of Massachusetts (Air Force Center for Environmental Excellence, 1997, 1998a) (fig. 26). This ground-water plume, known as the Storm Drain-5 (SD-5) plume, primarily consists of TCE with concentrations as high as 66,000 mg/L. Investigations by the MMR's Installation Restoration Program (IRP) suggested that the SD-5 plume was discharging to Johns Pond (Air Force Center for Environmental Excellence, 1998b). The MMR Installation Restoration Program, in cooperation with the USGS, sought to confirm that the SD-5 plume was discharging to the pond and to delineate the extent of the discharge area.

The Cape Cod aquifer near Johns Pond consists of about 250 ft of glacial outwash sand and gravel. The sediments are texturally uniform laterally and vertically. Johns Pond is a ground-water flow-through glacial kettle pond in this sand and gravel outwash plain. Ground water generally flows into the pond near its western side and discharges back into the ground near its eastern side, as indicated by the water-table contours on figure 26.

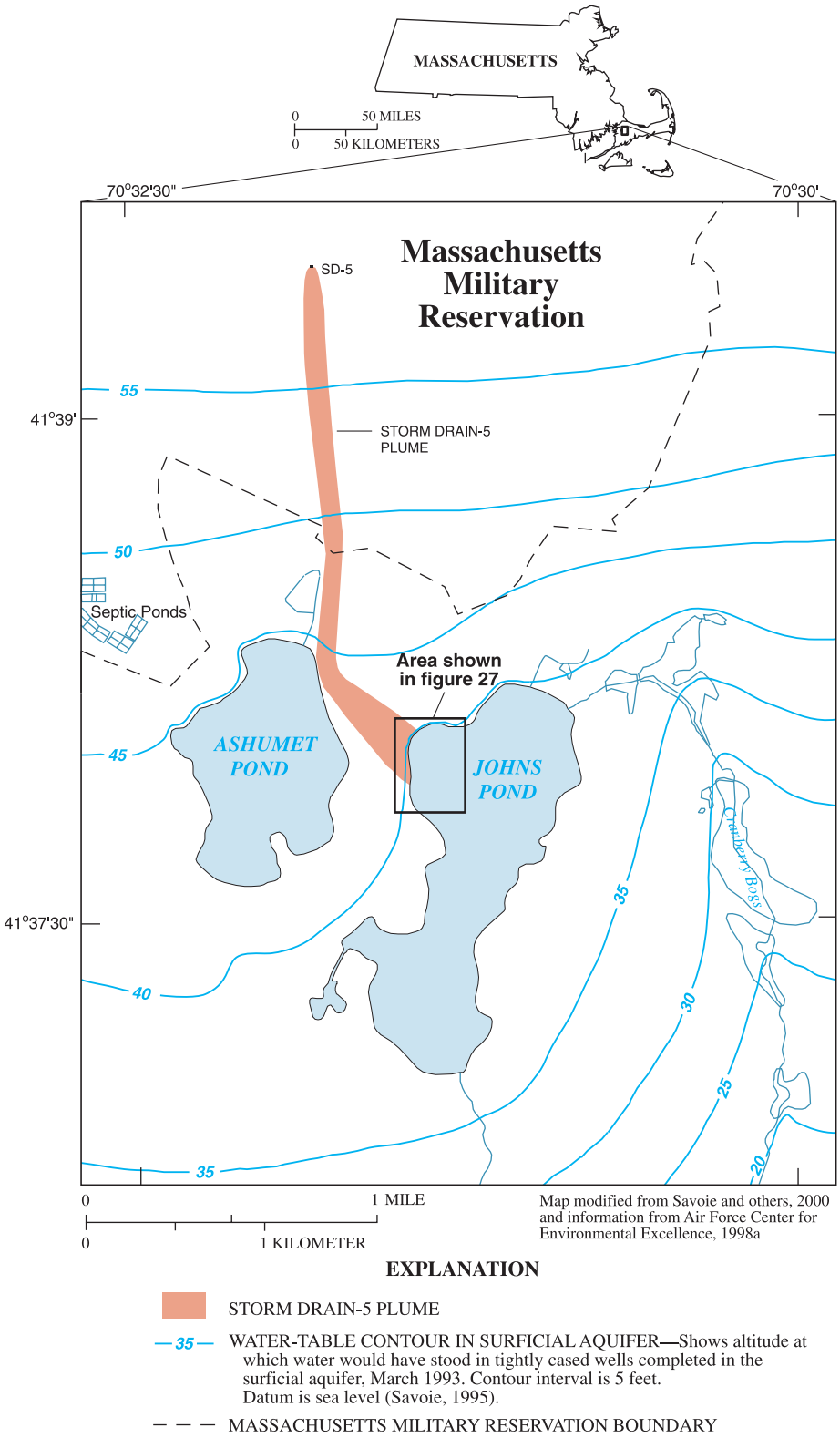


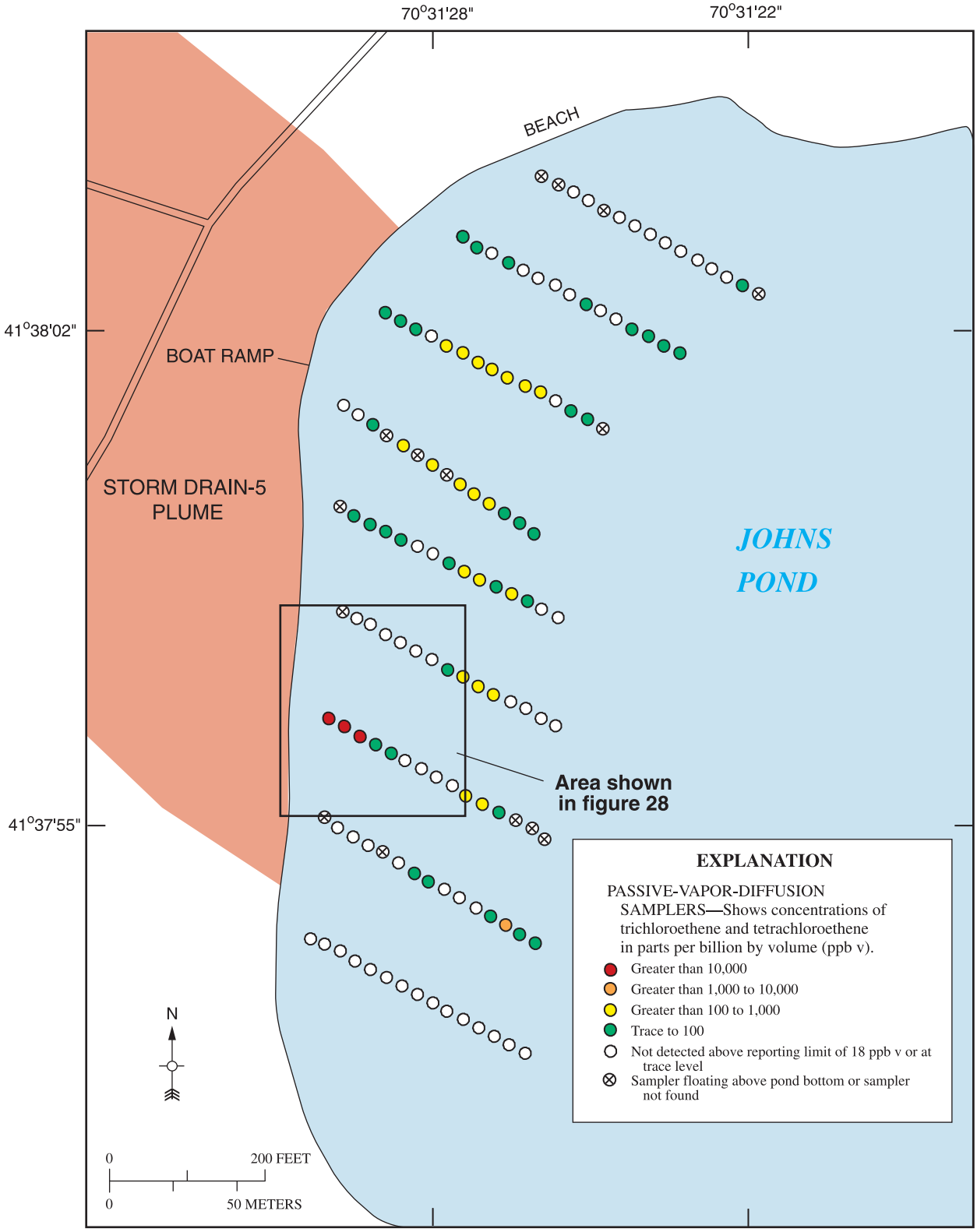
Figure 26. Locations of the Johns Pond study area and Storm Drain-5 contaminant plume, and the altitude of water table (March 1993), Cape Cod, Massachusetts.

Purpose and Design of Sampling

In this study, PVD samplers were installed in the bottom sediments of Johns Pond, to confirm that VOCs from the SD-5 plume emanating from the MMR were discharging into the pond (Savoie and others, 2000). In July 1998, an array of 143 PVD samplers was buried about 0.5 ft below the pond bottom in the presumed discharge area of the SD-5 plume and left in place for about 2 weeks to equilibrate (fig. 27). Divers installed samplers at water depths of 5 to 30 ft in Johns Pond. The lines of samplers extended a short distance into an area of fine grained bottom sediments, presumed to be the extent of most ground-water discharge. In November 1998, a second more closely spaced array of 119 PVD samplers was deployed on the basis of interpretation of data collected in August 1998.

Results

Data from the PVD samplers indicated two areas of high VOC concentrations. Samples from the first area contained TCE and PCE with concentrations in vapor as high as 890 and 667 ppb v, respectively (fig 27). This discharge area is about 1,000 ft wide, extends from 100 to 350 ft offshore, and is interpreted to be the discharge area of the SD-5 plume. Lines of samplers were long enough, by chance, to define the shape of the discharge area. Samples from the second area were closer to shore than the discharge area of the SD-5 plume and contained vapor concentrations of TCE as high as 47,000 ppb v. Ground-water samples collected with a drive-point sampler near this location confirmed the presence of TCE with concentrations as high as 1,100 mg/L. The array of PVD samplers deployed in November 1998 was centered around the area of high TCE concentrations to map this presumed separate plume (fig. 28). The discharge area detected with the PVD samplers retrieved in December 1998 was about 75 ft wide and extended from about 25 to 200 ft offshore. Vapor concentrations of TCE in this area were as high as 42,800 ppb v. Subsequent drilling by MMR Installation Restoration Program consultants confirmed that the TCE plume appears to be another plume that originates northwest of Johns and Ashumet Ponds and travels underneath Ashumet Pond (Air Force Center for Environmental Excellence, 1999, 2001) (fig. 29). Because of variations in ground-water-flow patterns laterally and with depth, this plume enters the area of Johns Pond from a different direction than the SD-5 plume.



Map modified from Savoie and others, 2000

Figure 27. Concentrations of trichloroethene plus tetrachloroethene in passive-vapor-diffusion samplers installed in pond-bottom sediments adjacent to the Storm Drain-5 contaminant plume, Johns Pond, Cape Cod, Massachusetts, August 1998.

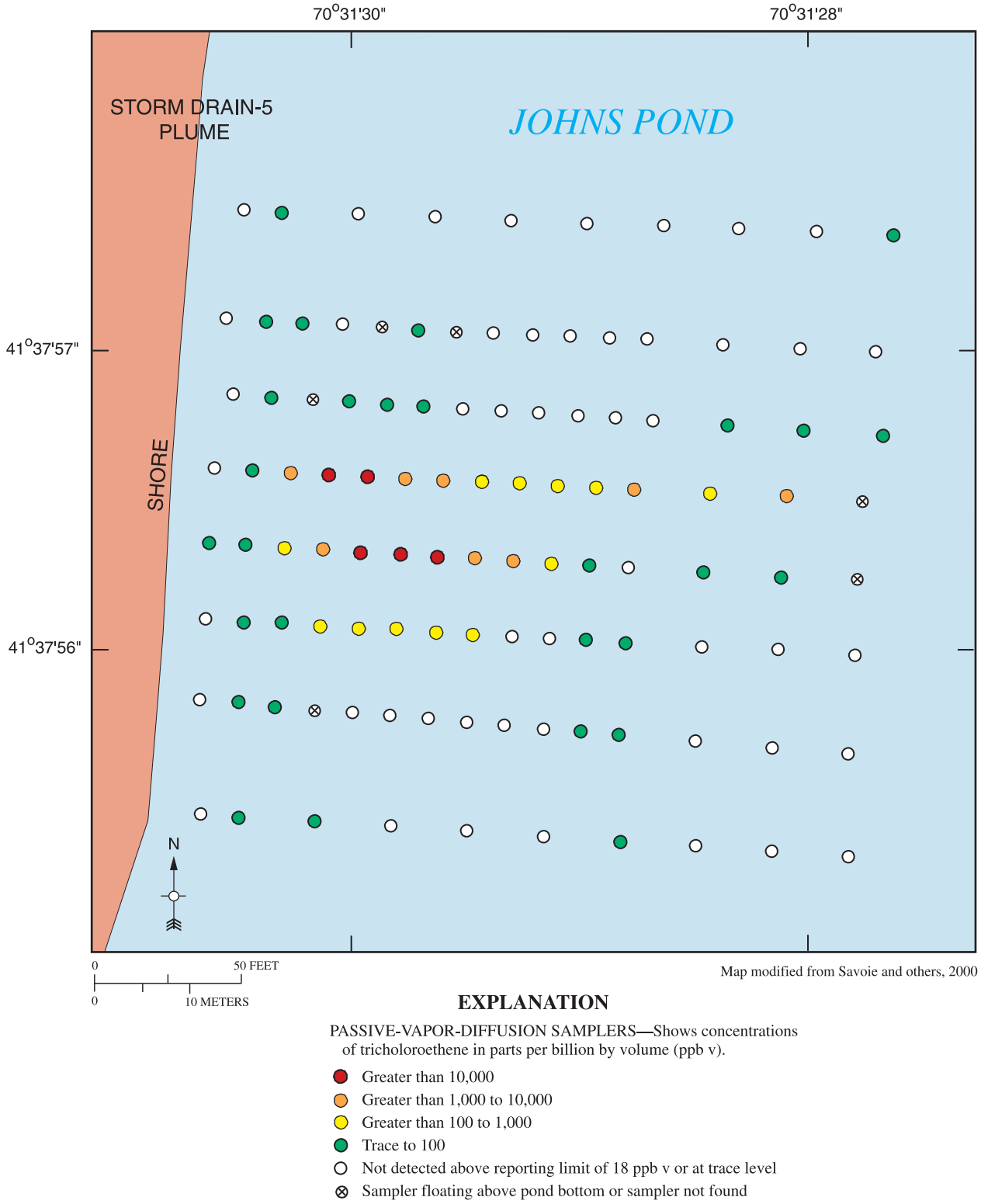


Figure 28. Concentrations of trichloroethene in passive-vapor-diffusion samplers installed in pond-bottom sediments in the zones where high concentrations (greater than 10,000 parts per billion by volume) of trichloroethene were detected with passive-vapor-diffusion samplers in August 1998, Johns Pond, Cape Cod, Massachusetts, December 1998.

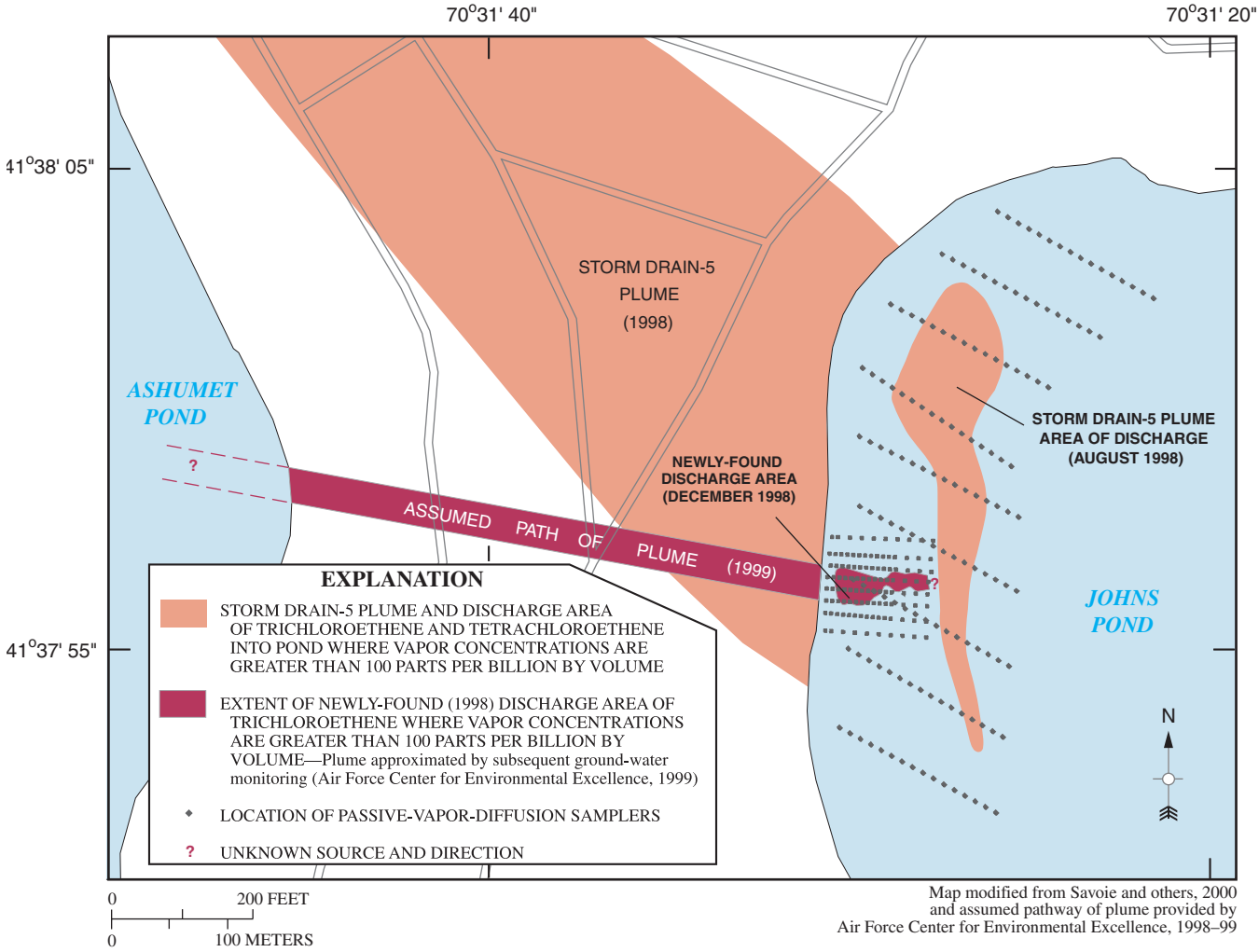


Figure 29. Discharge areas delineated with passive-vapor-diffusion samplers, August and December 1998, and ground-water pathways of the Storm Drain-5 plume and trichloroethene plumes, Johns Pond, Cape Cod, Massachusetts.

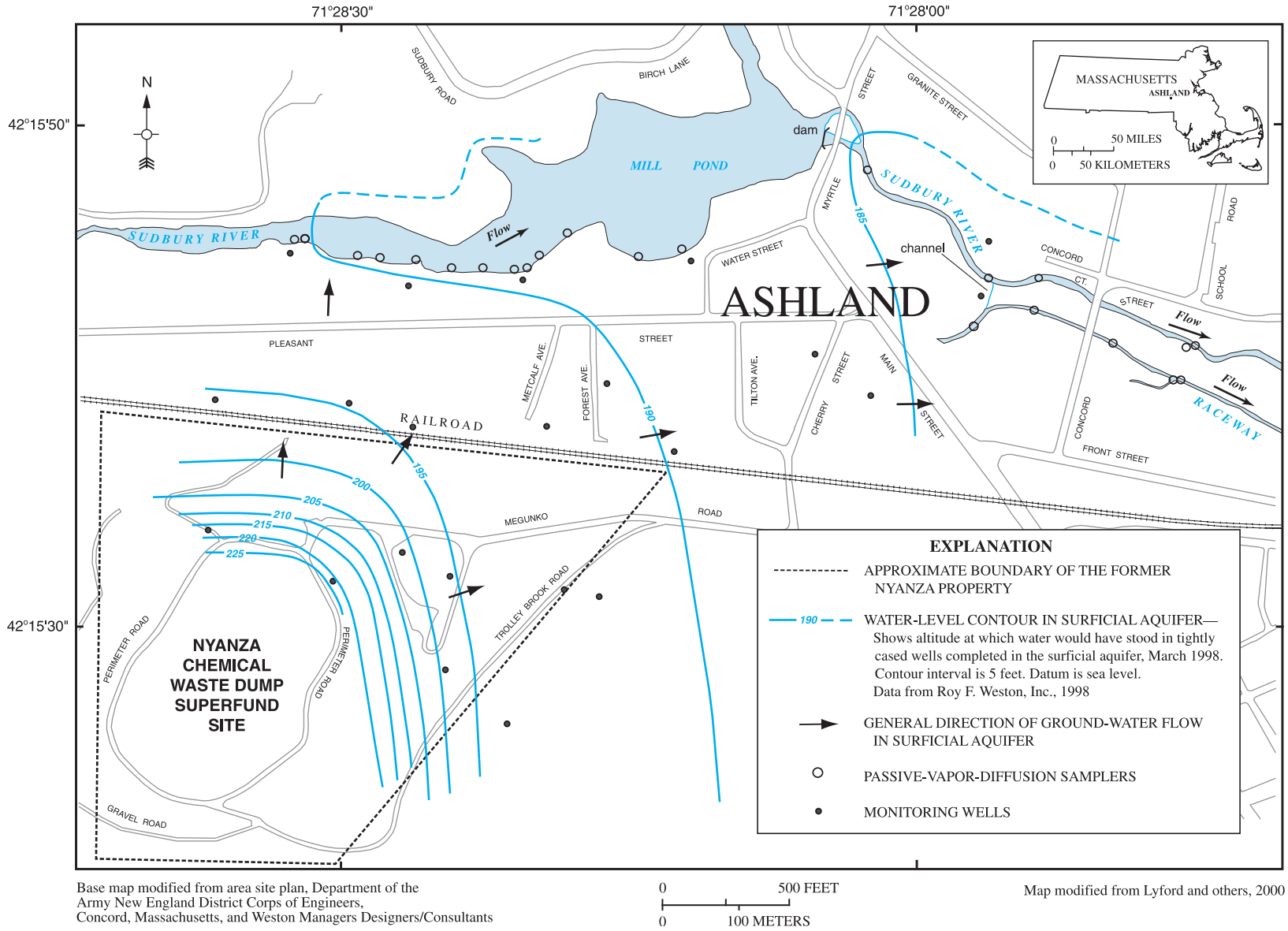
NYANZA CHEMICAL WASTE DUMP SUPERFUND SITE, ASHLAND, MASSACHUSETTS

By Forest P. Lyford, Richard E. Willey, *and* Sharon M. Hayes

Description of Study Area

The Nyanza property, part of the Nyanza Chemical Waste Dump Superfund site, is a parcel of land in Ashland, Massachusetts (fig. 30), where from 1917 to 1978, several textile dye manufacturers disposed of various waste products. Some of the wastes entered the ground-water system and formed a plume that extends to the Sudbury River and a nearby former mill raceway (fig. 31) (Roy F. Weston, Inc., 1998).

The ground-water system includes a surficial aquifer of glacial lake deposits and till, and a bedrock aquifer of fractured granite. The glacial lake deposits range in grain size from silt to coarse sand and gravel. The thickness of the fine-grained glacial lake sediments increases eastward, and the depth to bedrock increases eastward from less than 30 ft in the upstream end of the mill pond area to about 80 ft near the upstream end of the mill raceway. Most of the Superfund site is on till-covered bedrock, and the Sudbury River is on silt, sand, and gravel (Ebasco Services, Inc., 1991).



Base map modified from area site plan, Department of the Army New England District Corps of Engineers, Concord, Massachusetts, and Weston Managers Designers/Consultants

Map modified from Lyford and others, 2000

Figure 30. Location of Nyanza Chemical Waste Dump Superfund Site, passive-vapor-diffusion sampler locations, potentiometric-surface contours for the surficial aquifer, and directions of ground-water flow, Ashland, Massachusetts

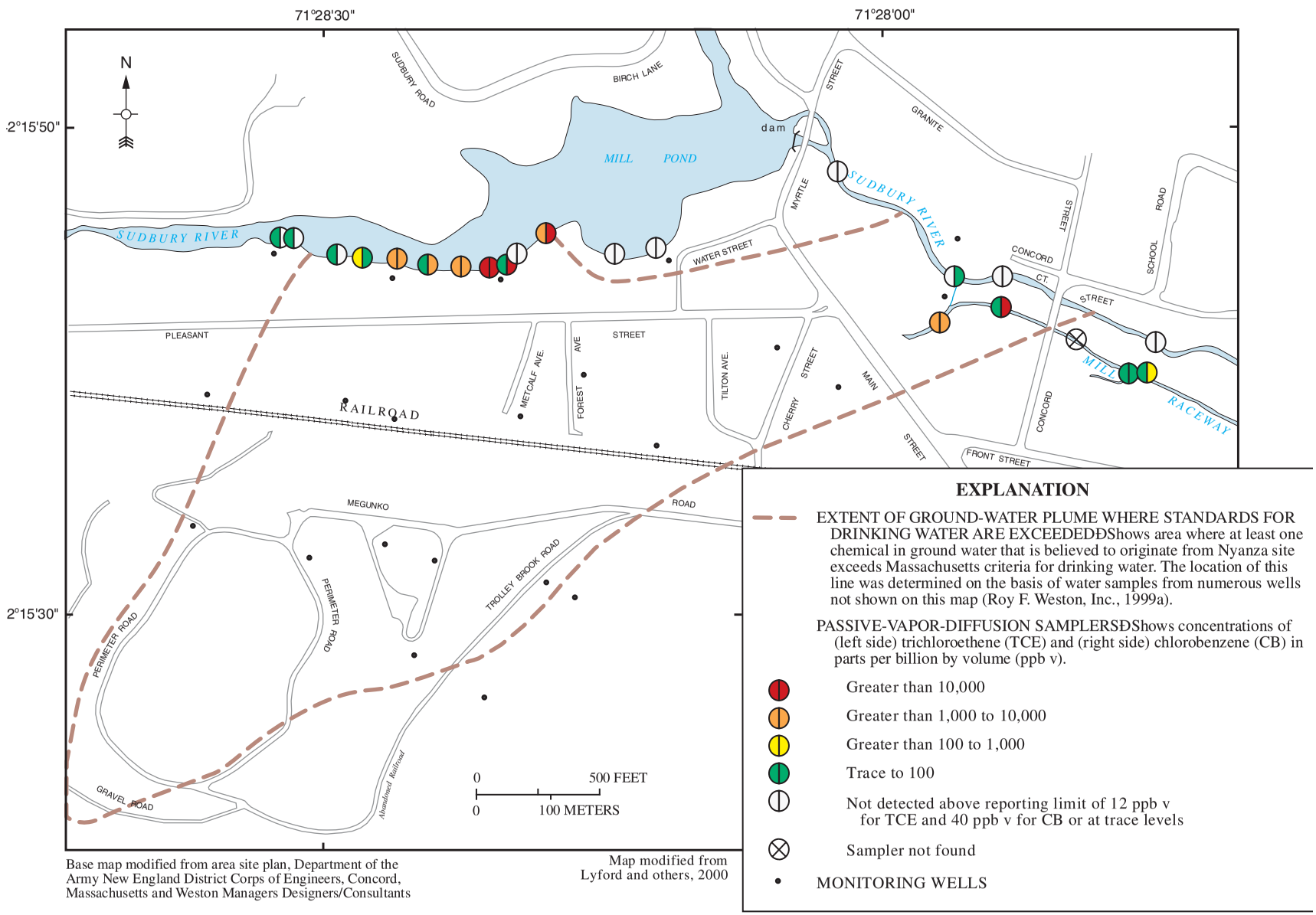


Figure 31. The extent of contaminants in ground water and concentrations of chlorobenzene and trichloroethene detected in passive-vapor-diffusion samples, Nyanza Chemical Waste Dump Superfund Site, Ashland, Massachusetts, February 1999.

A potentiometric surface map for the surficial aquifer (fig. 30) indicates that ground water flows northward from the Nyanza property to the Sudbury River and Mill Pond and eastward to the Sudbury River and former mill raceway downstream from the dam that forms Mill Pond (Roy F. Weston, Inc., 1998). A plume of contaminants in the surficial and bedrock aquifer system follows the ground-water-flow direction (fig. 31). Contaminants detected in ground-water monitoring wells near the river include the VOCs 1,1,1- trichloroethane, benzene, chlorobenzene, *cis*-DCE, PCE, TCE, and vinyl chloride. Chlorobenzene, TCE, and cis-DCE are the VOCs most commonly detected in ground water in the area of the plume. Also detected in ground water are mercury and the semi-volatile organic compounds (SVOCs) 1,2,4-trichlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene (Roy F. Weston, Inc., 1999a). Contaminants were not detected in monitoring wells near the downstream segment of the mill pond area, where water-level data show the pond is a source of recharge to ground water (Roy F. Weston, 1999b) (fig. 31).

Purpose and Design of Sampling

PVD samplers were used near the Nyanza property to accomplish three objectives (Lyford and others, 2000):

1. Determine if the distribution and concentrations of VOCs detected in samples from PVD samplers placed in stream-bottom sediments are consistent with the previously mapped distribution of contaminants in ground water near the river and former mill raceway.
2. Determine the time needed for VOCs in bottom sediments to re-equilibrate after installation of the samplers at this site.
3. Determine if PVD samplers might serve as alternatives to other sediment-pore-water sampling techniques, specifically seepage meters and whole sediment samples, to characterize the occurrence of VOCs in stream-bottom sediments.

To accomplish the first objective, PVD samplers were placed at 22 locations along the south bank of the Sudbury River in the area of Mill Pond and along the Sudbury River and raceway downstream from Mill Pond Dam. Samplers were deployed during January 19 through 20, and retrieved on February 16, 1999. To accomplish the second objective, two clusters of three PVD samplers each were placed at two sites. One PVD sampler from each cluster was retrieved at 1-week intervals and transported to USEPA's Lexington, Massachusetts, laboratory for analysis. To accomplish the third objective, PVD samplers were placed at locations selected by USEPA to compare analytical results with analyses of sediments and pore water extracted from seepage meters (Lyford and others, 2000). The seepage meters were inverted segments of steel drums equipped with a nozzle on the top for extraction of water (Roy F. Weston, Inc., 1999a).

Results

The distribution of VOCs in ground water detected in samples from PVD samplers agrees well with the distribution of contaminants in ground water mapped on the basis of samples from monitoring wells (fig. 31). Low levels of TCE (less than 25 ppb v) in PVD samples at the location farthest upstream indicates that VOCs in ground water may extend somewhat further west than the plume shown in figure 31. The absence of VOCs in samples from samplers placed at the downstream segment of Mill Pond is consistent with water-level observations that this section of the pond acts as a recharge source to ground water. Although chemical data are limited along the Sudbury River downstream from the dam, the general absence of VOCs in PVD samples indicates that this river reach was not a major discharge area for contaminants in ground water at the time of the study. The presence of VOCs in PVD samples along the mill raceway, however, confirms the mapped extent of the contaminant plume in ground water and indicates that the raceway is a discharge area for contaminated ground water.

An evaluation of equilibration time for PVD samplers in bottom sediments disturbed during installation of samplers indicates that 3 weeks or more may be needed in some settings for equilibration. The results were inconclusive, however, because changes in river stage and discharge may have affected concentrations of VOCs. Also, concentrations of VOCs in sediments may vary over short distances, and sampling and analytical methods are imprecise.

A comparison of analytical results for PVD samplers to analytical results for water from seepage meters indicated that concentrations of chlorobenzene and TCE correlated well for the two sampling methods. A comparison of results from PVD samplers to chemical analyses of sediments indicated that concentrations of chlorobenzene and TCE correlated poorly for the two methods. At several locations, PVD samplers detected VOCs where they were not detected in sediment samples. The apparent absence of VOCs in sediment samples may have resulted from high quantitation limits for the analyses.

CENTREDALE MANOR RESTORATION PROJECT SUPERFUND SITE, NORTH PROVIDENCE, RHODE ISLAND

By Peter E. Church, Forest P. Lyford, *and* Anna F. Krasko

Description of Study Area

At the Centredale Manor Restoration Project Superfund Site in North Providence, Rhode Island, the location of a former chemical company and a drum reclamation company, PCBs, dioxin, SVOCs, and VOCs have been detected in soils, and VOCs have been detected in ground water (A.F. Krasko, U.S. Environmental Protection Agency, written commun., 1999). The study area is an elongated area of about 12 acres along the eastern bank of the Woonasquatucket River just downstream of the U.S. Route 44 bridge (fig. 32). A former mill raceway that is about 1,900-ft long and located several hundred feet east of the river forms the approximate eastern boundary of the study area (fig. 33). The southern boundary of the study area is 50 ft downstream of the confluence of the mill raceway and the Woonasquatucket River, about 2,250 ft downstream from the U.S. Route 44 bridge. A cross channel, about 175-ft long, connects the river to the mill raceway about 600 ft upstream from this confluence.

Monitoring wells, installed in the northern part of the site in March 1999, encountered a top layer of fill, 3 to 6 ft thick, composed of silt, sand, gravel, and fragments of bricks, concrete, and wood. The fill is underlain by 3 to more than 8 ft of sand and gravel,

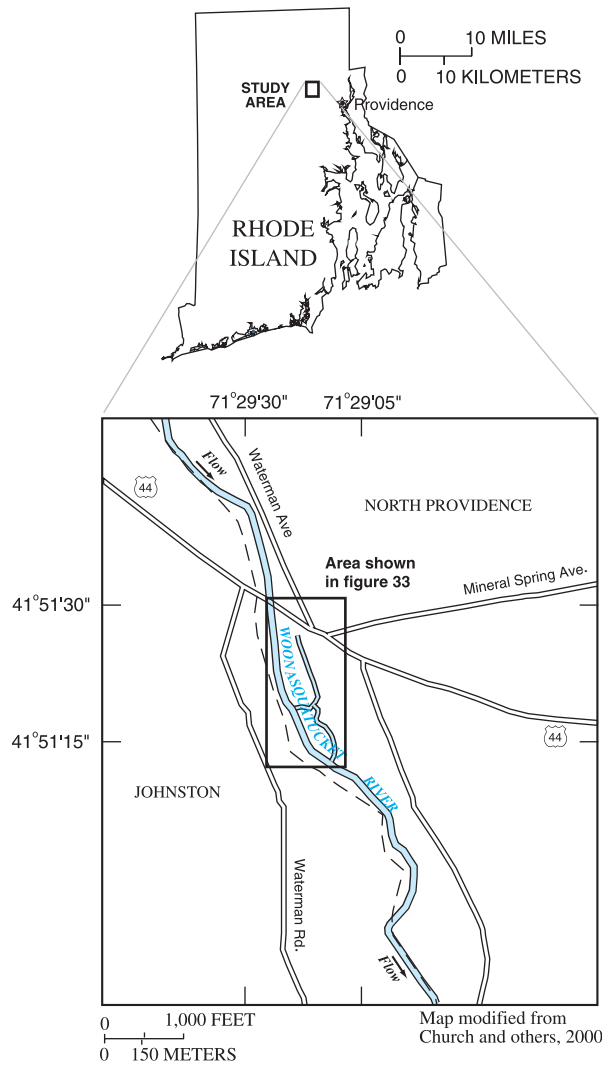


Figure 32. Locations of the Centredale Manor Restoration Project Superfund Site and study area, North Providence, Rhode Island.

which, in turn, is underlain by silty, gravelly sand, described as till of unknown thickness (A.F. Krasko, U.S. Environmental Protection Agency, written commun., 1999). The water table at the time these wells were drilled ranged from 2.6 to 7.5 ft below land surface. A potentiometric surface map is not available for this site. From June to November 1999, the USEPA collected numerous soil samples in the study area and detected dioxin, PCBs, VOCs, and SVOCs. The occurrence and distribution of contaminants in ground water had not been characterized at the time of this study.

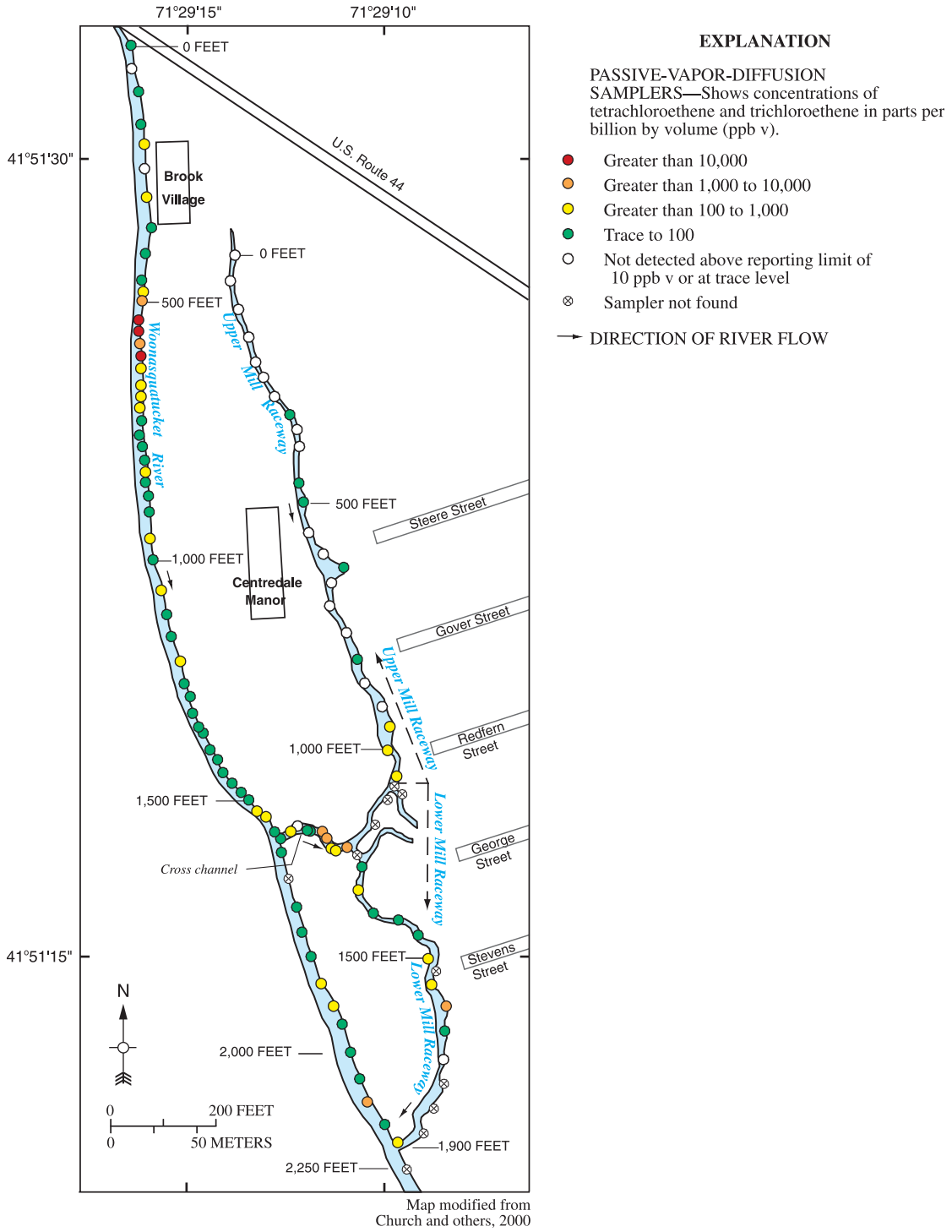


Figure 33. Concentrations of trichloroethene plus tetrachloroethene in passive-vapor-diffusion samplers installed in channel-bottom sediments of the Woonasquatucket River, a former mill raceway, and a cross channel, Centredale Manor Restoration Project Superfund Site, North Providence, Rhode Island, September 1999.

Purpose and Design of Sampling

On September 8 and 9, 1999, 115 PVD samplers were installed along the river, raceway, and cross channel to identify possible discharge areas of VOC-contaminated ground water and for a preliminary evaluation of the distribution and concentrations of VOCs and contaminant pathways in ground water (Church and others, 2000). The distance between samplers was 50 ft, except in reaches of the river and cross channel where the USEPA had indicated possible discharge of contaminants; in these locations, samplers were placed at intervals of 25 ft or less.

On September 21 and 22, 1999, the PVD samplers were retrieved. Sixty of the 62 samplers installed in the Woonasquatucket River were retrieved despite 2 near-flood flows in the 2 weeks after they were installed, which is most likely when the 2 samplers were lost. Nine of the 19 samplers installed in the lower section of the mill raceway were not found. Most likely these samplers were either washed away or buried in recently re-worked streambed sediments caused by high flows. All of the samplers installed in the upper section of the mill raceway and in the cross channel were retrieved. Target compounds for analysis, selected on the basis of soil-sample data, were benzene, ethylbenzene, toluene, *meta/para*-xylene, *ortho*-xylene, chlorobenzene, PCE, TCE, and 1,1,1-trichloroethane.

Results

VOCs were detected in 58 of the 60 PVD samplers placed in the river, 10 of the 24 samplers in the upper mill raceway, 9 of the 10 samplers from the lower mill raceway, and 9 of the 10 samplers in the cross channel. The compounds TCE and PCE were the principal VOCs detected of the nine target compounds, and vapor concentrations of these two compounds were generally less than 100 ppb v (fig. 33). Higher vapor concentrations, however, were detected along short reaches of these waterways. Vapor concentrations of TCE+PCE in samplers placed in the Woonasquatucket River about 500 to 600 ft downstream of the U.S. Route 44 bridge ranged from about 4,000 to 1,600,000 ppb v (fig. 33). The high vapor concentrations in this short reach, compared to vapor concentrations in river-bottom sediments upstream and downstream and in the former mill raceway and cross channel indicate that this is a major discharge area of contaminated ground water. The compounds TCE and PCE were detected in most PVD samplers downstream of this discharge area to the outlet of the mill raceway, but concentrations of these samples were much lower. These concentrations may reflect discharge of less contaminated ground water, especially in the approximate 350 ft reach of the river above the mill raceway outlet, or may represent mixing of contaminated river water with sediment-pore waters. Concentrations of TCE+PCE greater than 100 ppb v also were detected in the lower part of the upper mill raceway, in the lower mill raceway, and in the eastern part of the cross channel, indicating possible discharge areas of contaminated ground water (fig. 33). Nondetect or trace levels of VOCs immediately downstream of Route 44 suggest minimal contributions of VOCs from upgradient sources.

QUALITY-ASSURANCE PROCEDURES

Quality-assurance procedures for PVD sampling in New England were designed to help explain spurious detections of VOCs or anomalously high or low concentrations, if any, that would be difficult to explain on the basis of available site information. For all studies reported here, the primary objective was to identify possible discharge areas for VOCs in ground water. For this objective, the main quality concern was detections in PVD samplers where VOCs were not present and nondetections where VOCs were present. To help evaluate the concern that the sampling or analytical technique might cause detections of VOCs where they were not present, samplers were placed in areas where contaminants were not likely, such as upstream from or upgradient from mapped contaminant plumes in ground water. For all studies, numerous samples indicated that VOCs were not present in detectable quantities where they were unlikely to be present in ground water.

Duplicate samples were collected to help address the concern of false VOC detections where they were not present or false nondetections where they were present. Analyses of numerous samples that indicated concentrations below or above detection limits were confirmed with duplicate samples. Of the 437

duplicate-samples analyses (number of duplicate samples times the number of target compounds), a VOC was not detected above reporting limit in either sample in 343 duplicate samples; a VOC was detected above the reporting limit in both samples in 83 duplicate samples; a VOC was detected above the reporting limit in one sample but not the other in 11 duplicate samples (table 3). In 6 of the 11 exceptions, where a VOC was detected in one of the samples, but was not in the other, the highest concentration was less than 100 ppb v.

The concentrations of VOCs detected in PVD samplers for some sites provided useful information about the relative magnitude of concentrations of VOCs that might be expected at the ground-water and surface-water interface. For this use of the data, results from duplicate samples generally provided assurance that concentrations detected in samples were reasonable for that point sampled. A relative percent difference of 30 percent is commonly used to evaluate measurement performance in screening methods. A summary of relative percent differences between duplicate samples where a VOC was detected in both samples is shown in table 4. The relative percent difference for most duplicate samples analyzed for chlorinated VOCs (PCE, TCE, and chlorobenzene) were within 30 percent. For unknown reasons, however, a lower percentage of samples analyzed for petroleum compounds were within the 30 percent criteria for relative percent difference.

Trip blanks and equipment blanks also were used in some places to determine if contaminants were introduced during transport or during capping of sampler vials. No VOCs were detected in any of these samples except for a low concentration of toluene in one sample. The detection of toluene did not compromise the result observed for that site

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Table 3. Number and distribution of duplicate samples from the nine study sites in New England

[Number of duplicate sample analyses is the number of duplicate samplers deployed multiplied by the number of target compounds]

Study site	Number of duplicate sample analyses	Concentration detected above reporting limit in both samples	Concentration not detected above reporting limit in both samples	Concentration detected above reporting limit in only one sample
Eastern Surplus Company Superfund Site, Meddybemps, Maine	12	4	8	0
McKin Company Superfund Site, Gray, Maine	12	8	4	0
Nutmeg Valley Road Superfund Site, Wolcott and Waterbury, Connecticut	56	8	45	3
Baird & McGuire Superfund Site, Holbrook, Massachusetts	215	33	175	7
Allen Harbor Landfill, Davisville Naval Construction Battalion Center Superfund Site, North Kingstown, Rhode Island	24	1	23	0
Calf Pasture Point, Davisville Naval Construction Battalion Center Superfund Site, North Kingstown, Rhode Island	6	0	6	0
Otis Air National Guard/Camp Edwards Superfund Site, Johns Pond, Falmouth, Massachusetts	36	12	23	1
Nyanza Chemical Waste Dump Superfund Site, Ashland, Massachusetts	20	6	14	0
Centredale Manor Restoration Project Superfund Site, North Providence, Rhode Island	56	11	45	0
Total	437	83	343	11

Table 4. Relative percent differences of volatile organic compound (VOC) concentrations in duplicate samples where a VOC was detected above the reporting limit in both duplicate samples from the nine study sites in New England

Volatile organic compound	Number of duplicate samples	Percent of relative percent differences of concentrations in duplicate samples	
		Less than or equal to 30 percent	Greater than 30 percent
Tetrachloroethene	13	92	8
Trichloroethene	37	81	19
Chlorobenzene	2	100	0
Benzene	10	60	40
Ethylbenzene	6	50	50
meta/para-Xylene	7	43	57
ortho-Xylene	4	75	25
Toluene	4	75	25

SUMMARY AND CONCLUSIONS

Passive-vapor-diffusion (PVD) samplers are designed for detecting and delineating areas of VOC-contaminated ground water discharging into surface-water bodies. A PVD sampler consists of an empty glass vial sealed inside a polyethylene membrane tubing that is permeable to many VOCs of interest, such as petroleum and chlorinated compounds, but is not permeable to water. Samplers are buried in the bottom sediment of surface-water bodies, at or below the transition zone between surface water and ground water; and VOCs in the adjacent pore water, if present, diffuse through the polyethylene tubing and equilibrate with concentrations of air in the empty vial.

Applications of PVD samplers at and near nine hazardous-waste sites in New England have demonstrated the effectiveness of this sampling method in several hydrologic settings, including rivers and streams, ponds, wetlands, and coastal shorelines through a variety of bottom sediments including sand, silt, clay, organics, gravel, and cobbles. Areas of VOC-contaminated ground-water discharge from known ground-water plumes were confirmed or refined with PVD samplers at all nine sites. Areas of VOC-contaminated ground-water discharge from previously unknown ground-water plumes were identified with PVD samplers at the following Superfund Sites: Eastern Surplus Company in Maine; Baird & McGuire and Otis Air National Guard/Camp Edwards (Johns Pond) in Massachusetts; and Centredale Manor Restoration Project in Rhode Island.

The samplers should remain in place until sufficient time has elapsed for the pore water to recover from the environmental disturbances caused by sampler deployment and for the samplers to attain sufficient VOC concentrations to fulfill the data-quality objectives of the study. If the data-quality objective is to locate a VOC-contaminated ground-water-discharge area, then the samplers may be recovered before they have completely equilibrated, if they have accumulated sufficient VOC concentration to identify the contaminant-discharge area. Field studies suggest that this can be accomplished after a deployment period of 8 days or less, and in as little as 24 hours in some environments.

Spacing of samplers and selection of sampler location are also important in achieving the data-quality objectives. A sampling strategy for detecting plumes of VOCs in ground water or refining plume boundaries typically requires preliminary knowledge about potential sources of VOCs and a conceptual model of pathways for contaminants in ground water. Sampling should extend well upstream and downstream from likely discharge areas. The studies in New England have demonstrated that plumes typically discharge well beyond a riverbank or shoreline on the plume side of the water body. In fact, samplers placed at the edge of the water body may not detect a plume. In small streams a few feet wide, samplers placed along the center of a stream are typically sufficient to map plumes in ground water. Most plumes in New England hydrologic settings are at least 100 ft wide where they enter a surface-water body, so a spacing of 50 to 100 ft should be adequate to detect the presence of VOCs. In large water bodies such as rivers and ponds, a grid of samplers spaced 50 to 100 feet apart would typically detect the presence of VOCs. If the sampling goal is to characterize local variations in concentrations of VOCs, a shorter spacing may be needed.

The ability of PVD samplers to detect areas of discharging VOC-contaminated ground water depends on a variety of factors affecting contaminant discharge. These factors include the location and

lithologic heterogeneity of the discharge area, the orientation of the stream channel relative to the ground-water contamination, the offshore distance of the contaminant-discharge area, the potential temporal nature of the discharge-area location and discharging concentrations, and potential removal of VOCs by bed-sediment micro-organisms.

Two studies in New England (Lyford and others, 2000; Savoie and others, 2000) included co-located PVD and water-filled polyethylene bags described by Vroblesky (2001) to determine if concentrations of VOCs in pore water can be predicted from concentrations observed in PVD samplers. In theory, Henry's Law can be used to convert concentrations of VOCs in vapor to concentrations in water. Results of the two studies cited indicated that the use of PVD samplers for this purpose might be appropriate. Also needed, however, are temperature data measured with commercially available temperature probes for pore water at the sampling depth, and equilibration times of PVD samplers for the sediments in which the sample is obtained. In some settings, direct collection of pore-water samples, such as with small-diameter probes (Henry, 2000), may be more efficient than use of PVD samplers.

Several other types of information are useful for interpreting results from PVD sampling. It is helpful to know concentrations of VOCs in surface water. It is commonly assumed that the VOCs that discharge from ground water to surface water quickly volatilize to the atmosphere. In practice, however, VOCs persist downstream from a source and can compromise results of PVD sampling. Sampling of surface water upstream and downstream of the study area and at several points along a stream, depending on the length of the stream reach, is useful for interpreting PVD data from sediment-pore water. Surface-water data might be collected by suspending a sampler in surface water near the bottom of the water body or collecting water samples for head-space analysis on site or for standard laboratory analyses offsite.

It is also helpful to collect hydraulic head data at piezometers. Concurrent water levels in piezometers and surface water at the time of sampler deployment or retrieval will help determine if VOCs are discharged with ground water or accumulated in sediments from other sources. Continuous stage and ground-water-level data are also needed to detect changes in hydrologic conditions, such as a flood wave, that may affect VOC concentrations in sediments. Subsequent sampling may be desirable if hydrologic conditions changed appreciably during the sampling period.

Knowledge gained and lessons learned from the nine New England studies may be useful for others considering the application of PVD samplers. Results from these studies have provided insights on ground-water-flow patterns near surface-water bodies. Variations of VOC concentrations over short distances within areas of ground-water discharge were detected at several sites, which suggests local variations in contaminants at the contaminant source and possible local variations in ground-water-flow patterns. Discharge of VOC-contaminated ground water has been detected across the widths of rivers and streams. In one case, continued flow beneath the floodplain at a bend in the river resulted in VOCs being discharged through the bottom sediments to the opposite bank further downstream. Results at one site reinforced concepts about gaining and losing reaches in a mill-pond area and indicated that a former mill raceway was the principal discharge area for contaminated ground water downstream from the mill pond. Numerous detections of VOCs within a tidal zone near a landfill supported the concept that much of the shallow ground-water discharges in the tidal zone. The absence of VOCs in another tidal zone where VOCs are known to be present at depth suggests that the deep ground water discharges further offshore. The effect of surficial geology on ground-water discharge to surface-water bodies was observed at one site where the area of ground-water discharge from a deep surficial aquifer was affected by the lateral extent of an overlying confining lacustrine deposit.

Concentrations of VOCs in PVD samplers placed in river-bottom sediment downstream from the likely extent of a plume, but also in areas where VOCs were detected or are likely to be in surface water, may indicate an exchange of water between the surface water and bottom sediments. In this situation, surface-water sampling is needed, as well as the use of PVD samplers in the bottom sediments of the surface-water body. This additional sampling will help determine if VOCs in surface water have affected the concentrations of VOCs detected with the PVD sampler.

The absence of VOCs in PVD samplers does not exclude the possibility that VOCs are present in ground water. For at least two studies, VOCs were not detected

in some areas where they were known to be present in ground water. Local flow conditions may have diverted the discharge of contaminated ground water in these areas, or surface water may have been the principal source of water in bottom sediments. Where VOCs are suspected but not detected in PVD samplers, ground-water sampling may be needed for confirmation. The absence of VOCs at the ground-water/surface-water interface in areas of known ground-water contamination may indicate that surface water is a source of recharge. It may also indicate that discharge points for contaminated ground water are outside the area of investigation. This information is useful for further characterization of ground-water contamination and contaminant pathways.

Results from PVD samplers provide a qualitative assessment of VOC concentrations in ground-water plumes where they enter surface-water bodies. A fair correlation was observed between concentrations of VOCs in PVD samples and concentrations in water from co-located seepage meters. Several uncertainties, however, preclude estimating actual VOC concentrations in ground water from concentrations in vapor from PVD samplers. These uncertainties include equilibration times, variations in concentration over short lateral distances, variations in concentrations vertically (particularly at shallow depths), variations in temperatures at the ground-water and surface-water interface, and changing hydrologic conditions that affect ground-water-flow patterns and flow rates. These uncertainties, however, are not critical to successful application of the technique if the data-quality objective is simply to identify the presence of VOCs.

Quality-assurance procedures for PVD sampling help explain questionable detections of VOCs or unexpected high or low concentrations. For all studies in New England, numerous samples indicated that VOCs were not present in detectable quantities where they were unlikely to be present in ground water. Analysis of duplicate samples helped address the concern of false VOC detections where VOCs are not present, or false nondetections where VOCs are present. Numerous duplicate samples confirmed concentrations below or above detection limits. Duplicate samples also provided assurance that concentrations detected were reasonable for the point sampled. The relative percent difference for most duplicate samples analyzed for chlorinated VOCs were within 30 percent. For petroleum compounds, a lower percentage of samples analyzed were within the 30 percent criteria for relative percent difference. In some areas, analysis of trip blanks and equipment blanks helped determine if contaminants were introduced during transport or during capping of sample vials. VOCs were not detected in any of these samplers, except for a low concentration of toluene in one sampler, which did not compromise the result observed for that site.

Unexplored uses of PVD samplers include evaluation of chemical transformations at the ground-water/surface-water interface. These transformations can be evaluated by targeting degradation products during analysis of vapor or water, and by identification of areas of high concentrations of chemicals of environmental concern, such as semi-volatile organic compounds and metals, that are co-located with VOCs in ground water. After equilibration times for a particular setting are determined, PVD samplers also may help monitor concentrations of VOCs. Deploying PVD samplers could provide an alternative to installing wells, when a permanent well would present a safety hazard, such as to boats and swimmers, or where permanent wells would be subject to damage by vehicles or ice. Similarly, PVD samplers could be useful for studying how VOC concentrations change as hydrologic conditions change.

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Appendix 1. Laboratory and Field Testing of Passive-Vapor-Diffusion Sampler Equilibration Times, Temperature Effects, and Sample Stability

By Don A. Vroblesky

Laboratory and field tests were conducted to determine the time required for the vapor in the air-filled vials of the PVD samplers to equilibrate with concentrations of VOCs in the pore water of the adjacent sediment, and to determine the stability of VOC concentrations between the time of sample recovery and sealing of the sample vials. For the laboratory and field tests, the PVD samplers consisted of a 20-mL serum vial enclosed in a heat-sealed, 1.5-in. diameter LDPE tube. The vial was arranged such that a single layer of polyethylene was held tightly in place over the vial opening. The tubing was secured to the vial by a self-locking nylon tie. The assembly then was placed inside a second tube and heat sealed, trapping a minimum of air. Samplers used in the field were attached with self-locking nylon ties to a wire surveyor flag to mark the sampling site and to facilitate sampler recovery.

Upon recovery of the PVD samplers, the outer tube was cut open, leaving the inner tubing intact. A vial cap with a Teflon-coated stopper then was crimped onto the vial and inner bag. Vapor samples were obtained from the PVD samplers by inserting a syringe needle tip through the Teflon-coated stopper beneath the vial cap and extracting the vapor with a gas-tight syringe. Analysis of the the vapor was analyzed by photoionization detection with a Photovac 10SPlus gas chromatograph.

Equilibration Times and Temperature Effects

Equilibration times of PVD samplers under laboratory conditions were examined at 21°C and 10°C. For the test at 21°C, groups of three PVD samplers were added to 480-mL water-filled test jars spiked with a mix of VOCs at concentrations of approximately 20 to 100 µg/L each of *cis*-1,2-dichloroethene (*cis*-DCE), benzene, TCE, toluene, and PCE, in February 1998. The jars were stored at a 21°C for the duration of the test. For the test at 10°C three PVD samplers were added to each of fourteen 1.9-L test jars spiked with a mix of benzene (570 µg/L), toluene (520 µg/L), TCE (430 µg/L), and PCE (500 µg/L), in June 2001. The test jars were maintained at approximately 10°C by storing them in an incubator. Water temperatures in the jars were measured at each sampling time and ranged from 7.6 to 11.3°C (average of 10.2°C). The water-filled jars in both tests contained no headspace.

An additional test was done to compare differences in equilibrium concentrations at various temperatures. Standards of toluene and PCE were added to water in a 40-L container. The PVD samplers were placed in 1.9-L jars in groups of three, and the jars were filled with test water by submerging and capping the jars underwater in the 40-L container. The jars were stored at different temperatures. At various times, one jar from each temperature treatment was opened, the temperature was measured, the PVD samplers were capped, and a water sample was collected for toluene and PCE laboratory analysis. Vapor samples from the PVD samplers were analyzed by headspace analysis. Water temperatures ranged from 0.2 to 4.1°C (average of 1.4°C) in the coldest treatment, from 7.9 to 10.8°C (average of 9.5°C) in the next coldest treatment, and from 19.4 to 24.6°C (average of 22.4°C) in the room-temperature treatment. Concentrations in water ranged from 210 to 310 µg/L of toluene and 110 to 340 µg/L of PCE.

Recovery of the PVD samplers at each sampling time consisted of opening the jar, removing the PVD samplers, cutting open the external LDPE bag, and sealing the PVD samplers with crimp-type caps with Teflon-faced seals. The test at 21°C involved 10 sampling times over approximately 59 hours (table 1*A*), the test at 10°C involved 13 sampling times and 1 duplicate over approximately 222 hours (table 1*B*), and the test at 3 temperatures involved 6 sampling times and 1 duplicate sample over 456 hours (table 1*C*).

In addition, the USGS conducted relatively short-term tests of PVD samplers deployed in streambed sediments in areas of VOC-contaminated ground-water discharge to examine sampler equilibration dynamics under field conditions. For these tests, the samplers were deployed in different environments. Site1 was in Coastal Plain sands at the Savannah River Site, South Carolina, in an area with a relatively high upward hydraulic gradient (0.3 ft/ft). The sediment at site 1 had a relatively large hydraulic conductivity of 21 to 65 ft/d (Nichols, 1993; Nichols and others, 1995; Phifer and others, 1995). Site 2 was in silty saprolite downgradient from a former waste-drum disposal site in a part of the stream with a relatively low upward hydraulic gradient (0.02 ft/ft).

Table 1*A*. Average concentrations and standard deviations of volatile organic compounds in passive-vapor-diffusion samplers over time at 21 degrees Celsius under laboratory conditions in 480-milliliter test jars with spiked concentrations of less than 100 micrograms per liter

[*cis*-DCE, *cis*-1,2-dichloroethene; TCE, trichloroethene; ppb, parts per billion]

Time, in hours	Number of samplers	Average concentrations, in ppb by volume				Standard deviation, in ppb by volume			
		cis-DCE	Benzene	TCE	Toluene	*cis*-DCE	Benzene	TCE	Toluene
0	3	0	0	0	0	0	0	0	0
0.75	3	158	223	118	146	23	77	52	75
1.75	3	431	498	171	110	124	175	73	40
2.75	3	654	939	271	218	159	393	103	119
5.75	3	687	1,054	297	276	192	300	71	50
10.75	3	1,416	2,058	492	565	315	669	209	316
23.75	3	1,970	3,101	813	913	14	64	26	27
31.75	3	1,880	3,044	802	975	68	121	66	122
51.75	3	1,853	2,923	732	929	54	86	29	52
58.75	3	1,705	2,747	695	879	34	58	10	24

Table1*B*. Average concentrations and standard deviation of volatile organic compounds in passive-vapor-diffusion samplers over time at 10 degrees Celsius under laboratory conditions in 1.9-liter test jars with spiked concentrations ranging from 430 to 570 micrograms per liter

[PCE, tetrachloroethene; TCE, trichloroethene; D, Duplicate test jar; NA, not applicable; ppb, parts per billion]

Time, in hours	Number of samplers	Average concentrations, in ppb by volume				Standard deviation, in ppb by volume			
		Benzene	TCE	Toluene	PCE	Benzene	TCE	Toluene	PCE
0	3	0	0	0	0	0	0	0	0
2.25	3	150	303	0	0	10	35	0	0
5.25	3	823	1,065	333	69	359	514	90	15
9.25	3	1,880	2,130	1,185	334	1,655	1,451	540	81
14.25	3	6,166	4,999	2,853	700	3,877	2,762	1,177	165
28.75	2	20,265	14,395	9,787	2,432	318	389	896	144
35.25	2	21,180	14,725	9,737	2,347	1,414	2,539	655	166
57.25	1	25,450	24,060	15,110	4,223	NA	NA	NA	NA
78.25	3	31,227	33,523	20,360	6,179	2,177	4,393	767	313
102.25	3	31,990	35,293	22,480	7,054	652	1,979	1,644	612
150.25	2	31,220	34,275	23,320	7,867	438	1,025	184	522
150.25 D	1	32,150	37,140	21,430	7,229	NA	NA	NA	NA
222.25	3	31,543	35,253	21,900	7,465	957	1,303	1,763	584

Table 1*C*. Ratio of concentrations from passive-vapor-diffusion sampler to aqueous-phase concentrations for toluene and tetrachloroethene over time at various temperatures under laboratory conditions in 1.9-liter test jars containing 210 to 310 micrograms per liter of toluene and 110 to 340 micrograms per liter of tetrachloroethene

[ppb v to µg/L, ratio of parts per billion by volume to micrograms per liter; °C, degrees Celsius; --, no samples]

Hours	Ratio of passive-vapor-diffusion to aqueous-phase concentrations (ppb v to µg/L)					
	Toluene			Tetrachloroethene		
	22.4°C	9.5°C	1.4°C	22.4°C	9.5°C	1.4°C
0	0.0	0.0	0.0	0.0	0.0	0.0
24	76.9	11.3	15.5	14.4	3.9	2.2
72	116.1	73.4	19.7	60.1	35.9	6.6
192	107.3	62.7	21.0	67.6	35.9	11.7
336	105.3	60.0	27.9	81.3	39.0	17.3
336	100.3	55.8	--	69.8	46.7	--
456	103.5	49.8	23.4	68.4	33.9	17.2

Hydraulic gradients at each site were determined by driving 1-in-diameter steel pipes into the streambed to depths of 1.5 and 3 ft. A bolt loosely seated into the downward end of the pipes prevented sediment from moving up into the pipe as it was driven into the sediment. The bolt then was driven out of the pipe to allow water to enter. After a few hours of equilibration, the water levels in the pipes were measured relative to the stream stage outside the pipes. These water levels provided an approximate measurement of the upward hydraulic gradient. At each field site, approximately 20 to 30 PVD samplers were buried in an area of approximately 6 ft^2. The samplers were recovered in groups of three at various times over approximately 50 hours.

Equilibration time for PVD samplers under field conditions depends on the time required by the PVD sampler to equilibrate with ambient water, and the time required for the contaminant distribution in pore water, disturbed by installation of the sampler, to return to ambient conditions. Laboratory tests presented here provide information regarding the time required by the PVD sampler to equilibrate with ambient water. Field data for this and other investigations involving various types of in-situ samplers can provide a better understanding of the time required for sediment-pore-water concentrations to equilibrate after disturbances caused by sampler deployment.

Temperature is one primary factor affecting the equilibration time of VOC movement across a polyethylene membrane. At 21°C under laboratory conditions, the time required for concentrations of *cis*-DCE, benzene, TCE, toluene, and PCE to stabilize was approximately 24 hours (fig. 1*A*, table 1*A*). At 10°C under laboratory conditions, concentrations of benzene, TCE, toluene, and PCE appeared to require about 102 hours to equilibrate (fig. 1*B*, table 1*B*). Equilibration times, therefore, increase as temperature decreases. This increase in equilibration time with decreasing temperature is consistent with the general trend previously shown for sampling major ions and nutrients with dialysis samplers (Carignan, 1984). In these studies, equilibration times ranged from approximately 15 days in a warm (20–25°C) environment, and approximately 20 days in a cold (4–6°C) environment.

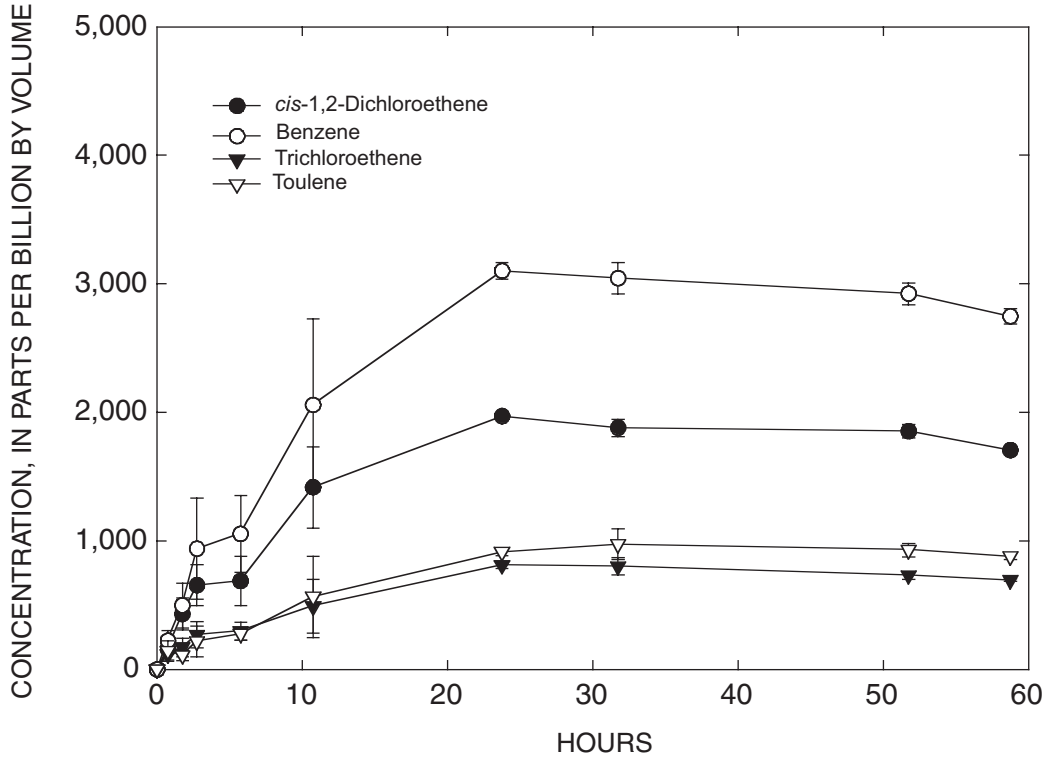

Figure 1*A*. Changes in concentrations of volatile organic compounds in passive-vapor-diffusion samples over time at 21 degrees Celsius under laboratory conditions in a mixed solution of volatile organic compounds with aqueous concentrations less than 100 micrograms per liter.

Temperatures also change the equilibrium distribution of VOCs between the aqueous and vapor phase. At cold temperatures, there is less of a tendency for volatilization than at warmer temperatures. For the same aqueous concentration, therefore, higher concentrations will be detected in PVD samplers at warm temperatures than at cold temperatures (fig. 1*C*, table 1*C*).

In contrast, differences in VOC concentrations between tests or sites theoretically should not produce different equilibration times. The concentration gradient between the inside and outside of the polyethylene membrane does affect the diffusion flux, as evidenced by Fick's Law; however, although a steeper concentration gradient results in an increased diffusion rate, the required amount of solute transfer is larger than in a lower concentration gradient. In effect, the equilibration time is the same for both situations. This fact can be seen in the formula for halftime of chemical uptake of organic compounds across a polyethylene membrane in semipermeable membrane devices (SPMDs):

$$t_{0.5u} = -\ln 0.5\ (K_{ow}\ V_L/R_S),$$

where $t_{0.5u}$ is the halftime to equilibration, K_{ow} is the octanol-water coefficient, V_L is the volume of the lipid sorbent, and RS is the volume of water sampled by the SPMD per day and is independent of concentration (Huckins and others, 1997).

Field tests for this investigation demonstrate that equilibration times can vary among field sites. At site 1 in South Carolina, the TCE concentrations in the PVD samplers approximately stabilized after about 12 to 24 hours (fig. 1*D*, table 1*D*). At site 2 in South Carolina, however, the TCE concentrations still were increasing at 47 hours (fig. 1*D*, table 1*D*). A field test in Massachusetts found that PVD samplers in sediments of the Sudbury River appeared to require 3 weeks or more to equilibrate (Lyford and others, 2000). These differences in equilibration times can result from a variety of factors. At site 1, the rate of water movement past the samplers was substantially larger than the rate

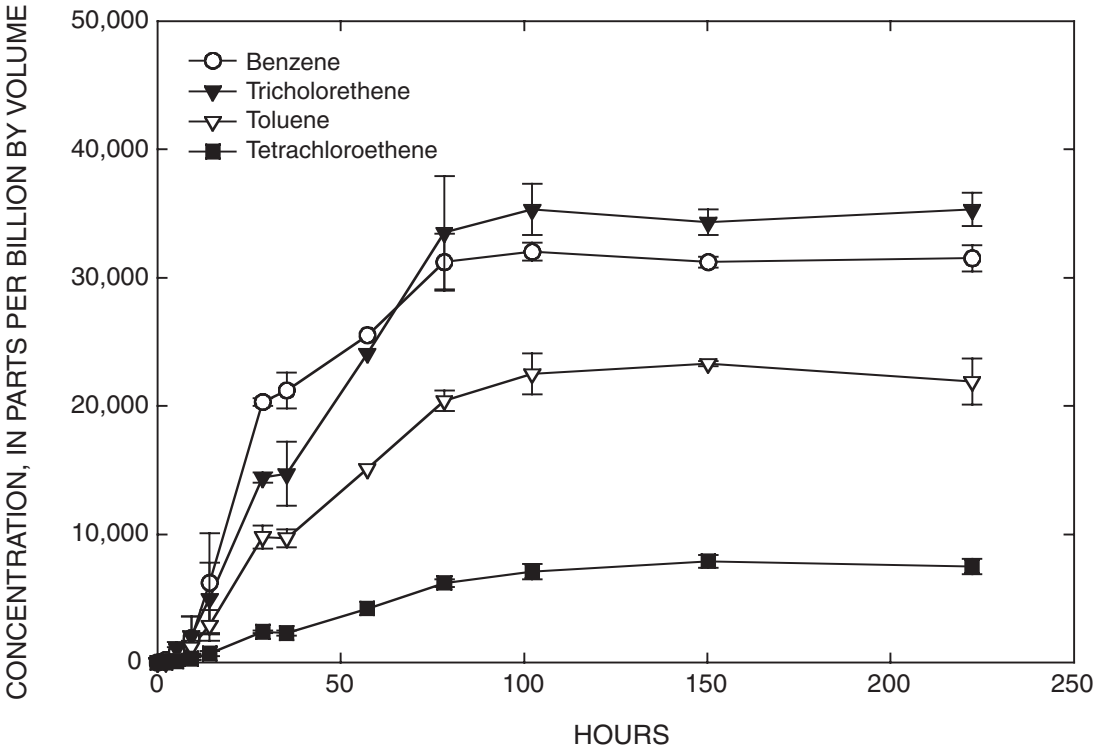

Figure 1*B*. Changes in concentrations of volatile organic compounds in passive-vapor-diffusion samples over time at 10 degrees Celsius under laboratory conditions in a mixed solution of volatile organic compounds with aqueous concentrations ranging from 430 to 570 micrograms per liter.

past the slower equilibrating samplers at site 2, as evidenced by the differences in permeability and hydraulic gradient (fig. 1*D*). The surface water introduced into the excavated sampler holes would have been more rapidly replaced by discharging ground water at site 1 than at site 2. Additionally, site 1 was sampled in early September, and site 2 was sampled two months later, in November. Colder water temperatures in November may have contributed to the decrease in equilibration time. The samplers from the Sudbury River in Massachusetts were recovered from fine-grained sediment in February 1999, in water that was substantially colder than at either of the South Carolina sites.

An important concept to remember in considering the length of equilibration time for field deployment, however, is that PVD samplers typically are used as a reconnaissance tool in surface-water sediments to locate areas of discharging ground water contaminated with VOCs. For this use, the mere presence or absence of target VOCs in samplers can provide practical information. At the field locations tested in South Carolina, the PVD samplers showed considerable concentrations of the target VOCs within 24 hours or less (fig. 1*D*). Despite the apparent lack of equilibration, the PVD samplers in the Sudbury River showed considerable concentrations by the first retrieval (8 days). Although the PVD samples had not equilibrated at all of the sites, the data from all of the sites were adequate to meet the objective of mapping contaminant-discharge areas. These data suggest that a deployment period of 8 days or less is adequate to provide data sufficient to locate major VOC discharge areas beneath surface water, and as little as 24 hours is sufficient at some sites.

If it is important for the data-quality objective that the PVD samples must have reached equilibrium at the time of sampler recovery, then the samplers may need to remain in place longer than 8 days, depending on the rate of ground-water movement and

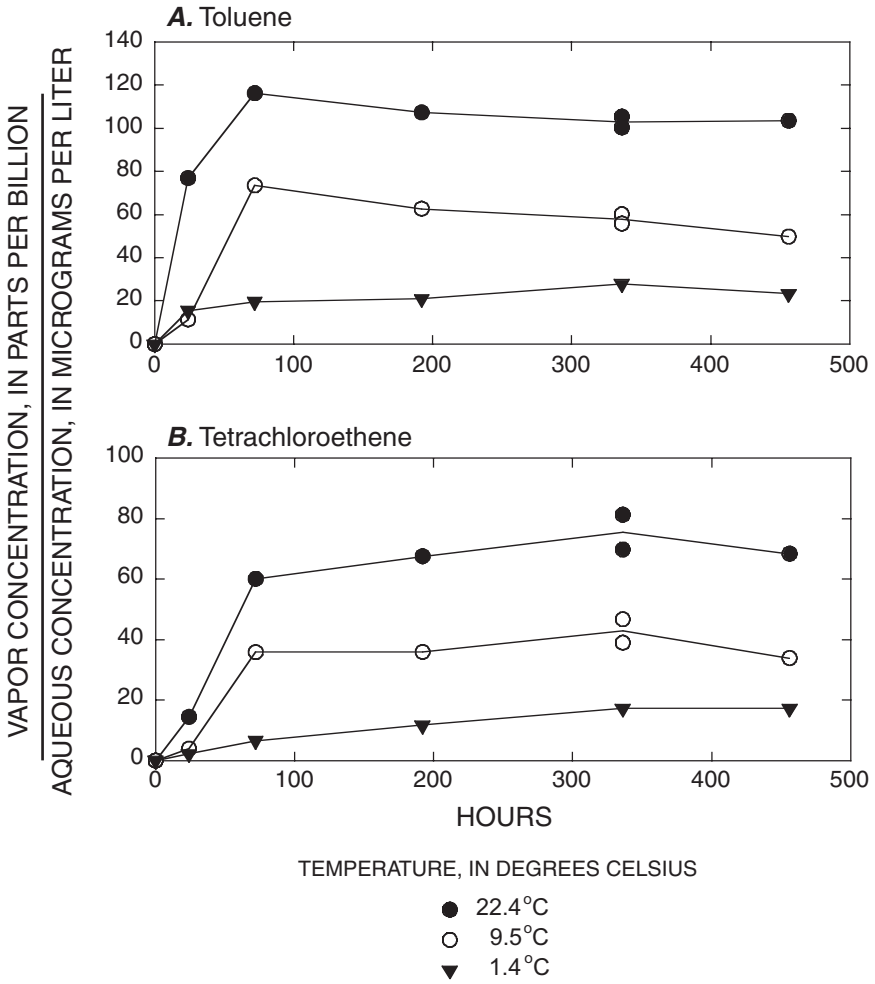

Figure 1*C*. Ratio over time of (*A*) toluene and (*B*) tetrachloroethene gas concentrations by volume (parts per billion) in passive-vapor-diffusion samplers to aqueous concentrations by mass (210 to 310 micrograms per liter of toluene and 110 to 340 micrograms per liter of tetrachloroethene) in a test solution containing the diffusion samplers in 1.9-liter jars at average temperatures of 22.4, 9.5, and 1.4 degrees Celsius.

the ground-water temperature. Some insight into equilibration times can be gained by examining passive-diffusion-bag (PDB) samplers, which are water-filled polyethylene diffusion samplers. Under laboratory conditions at 21°C, the PDB samplers equilibrate more slowly (approximately 48 hours; Vroblesky, 2000) than PVD samplers (approximately 24 hours); therefore, the field equilibration times of PVD samplers probably are no longer than those for PDB samplers under similar field conditions. One field investigation showed adequate equilibration of PDB samplers to aquifer TCE and carbon tetrachloride within 2 days in a highly permeable aquifer (Vroblesky and others, 1999). In other investigations, PDB samplers recovered after 14 days were found to be adequately equilibrated to chlorinated VOCs (Obrien & Gere Engineers, Inc., 1997a, 1997b; Hare, 2000); therefore, the equilibration time was 14 days or less under those field conditions. Because it appears that 2 weeks of equilibration time probably is adequate for many applications sin permeable formations, a minimum PVD-equilibration time of 2 weeks is recommended for discharge areas in sandy sediment.

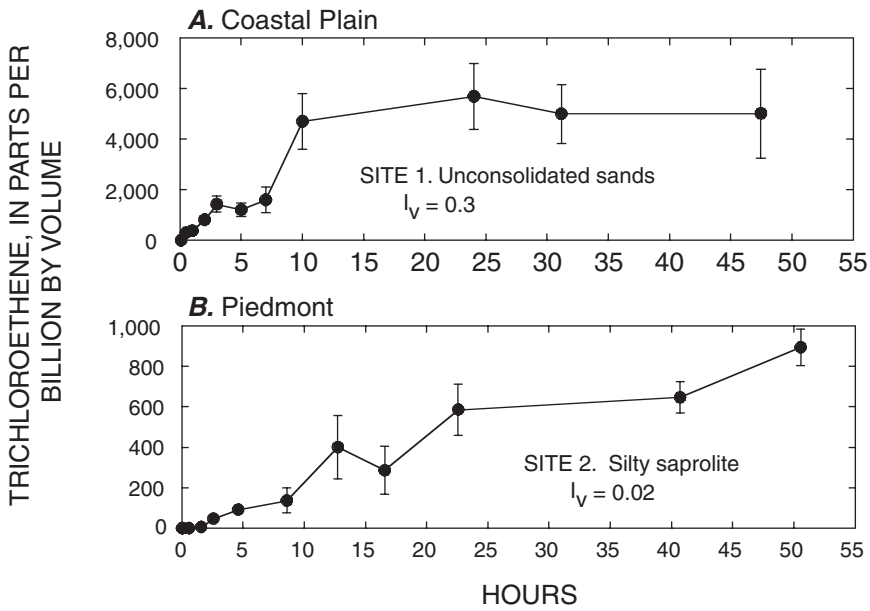

Figure 1*D*. Changes in trichloroethene concentrations over time in passive-vapor-diffusion samples from contaminated ground-water discharge areas in South Carolina in (Site 1) Coastal Plain sediments and (Site 2) Piedmont sediments with differing sediment types and vertical hydraulic gradients.

Equilibration of PVD samplers in fine-grained sediment may take longer than 2 weeks, as shown by the test in the Sudbury River (Lyford and others, 2000). Equilibration times for PVD samplers in poorly permeable sediment have not yet been determined. A confounding factor in determining equilibration times in such conditions is that flow conditions and possibly plume concentrations can vary with time and space, and these variations may be reflected in the PVD-sampler concentrations.

In summary, if the data-quality objective is to locate areas of VOC-contaminated ground-water discharge, then a deployment period of 8 days or less is adequate to provide data sufficient to locate major VOC discharge areas beneath surface water, and as little as 24 hours is sufficient at some sites. If it is important for the data-quality objective that the PVD samplers must have reached equilibrium at the time of sampler recovery, then the samplers may need to remain in place for about 2 weeks in sandy sediment and possibly longer than 3 weeks in poorly permeable sediment at cold temperatures.

Sample Stability

Laboratory tests also were conducted to determine the diffusion loss of VOCs in PVD samplers between the time of sampler recovery and sealing of the sampler vials. The samplers were allowed to equilibrate for 2 weeks in a water-filled container having mixed VOCs. The samplers then were removed from the water and allowed to stand at 21°C for various time intervals over a period of hours before capping. The vapor samples then were analyzed by photo-ionization gas chromatography.

Concentrations of benzene, TCE, and toluene in uncapped PVD samplers at 21°C did not substantially decrease over 60 minutes between sampler recovery and capping the sampling vials. These data suggest that VOC concentrations within the uncapped PVD samplers are relatively stable for at least 1 hour at 21°C under laboratory conditions. Under field conditions, however, abrasions and other factors may adversely affect the membrane. Consequently, it is strongly recommended that PVD samples be capped and sealed immediately upon recovery.

Table 1*D*. Average concentrations and standard deviations of trichloroethene over time in passive-vapor-diffusion samplers in bottom sediment of streams at contaminated ground-water-discharge areas in the Coastal Plain (site 1) and the Piedmont (site 2) of South Carolina, 1998

[TCE, trichloroethene; ppb, parts per billion; NA, not applicable]

Site 1				Site 2			
Hours after deployment	Number of samples	TCE concentration, in ppb by volume		Hours after deployment	Number of samples	TCE concentration, in ppb by volume	
		Average	Standard deviation			Average	Standard deviation
0	1	0	NA	0	1	0	NA
.08	3	5	4	.08	3	0	0
.5	3	307	60	1	3	0	0
1	3	378	146	2	3	6	6
2	3	815	117	3	3	47	19
3	2	1,431	313	4.6	3	92	21
5	3	1,208	270	9	3	136	61
7	3	1,601	516	12.75	3	400	156
10	3	4,710	1,103	17	3	286	120
24	3	5,693	1,300	23	3	586	127
31	3	5,002	1,167	41	3	647	78
47	2	5,019	1,758	50.5	3	894	91

Appendix 2. Field Screening of Volatile Organic Compounds Collected with Passive-Vapor-Diffusion Samplers with a Gas Chromatograph

By Scott Clifford, U.S. Environmental Protection Agency

1.0 Summary of Method

Field screening with a portable gas chromatograph (GC) provides tentative identification and estimated concentrations of volatile organic compounds (VOCs) in air samples. This screening technique can provide quick and reliable results to assist in important onsite decision making. An aliquot of the air/vapor sample is injected into a calibrated GC equipped with a photoionization detector and electron capture detector. Results indicating VOC detections and estimated concentrations are displayed on a chart recorder, a portable computer screen, or other data-collection system. Retention times, the time since injection of the sample into the GC to the time peak responses are recorded, are used for compound identification. The peak heights, or areas, are used to estimate concentrations of the identified compounds. Reporting levels (RL) can vary depending upon instrument performance and settings, or can be set on the basis of data quality objectives. Typical achievable reporting levels for many VOCs of interest are shown in table 2*A*. Concentrations are in units of parts per billion by volume (ppb v).

2.0 Scope and Application

The procedure described here is applicable to chemists performing screening for VOCs in air samples collected with passive-vapor-diffusion (PVD) samplers.

3.0 Definitions

3.1 FIELD DUPLICATES (FD1 and FD2): Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

3.2 HEADSPACE: Air above water standard in sample vial.

3.3 LABORATORY DUPLICATE (LD1 and LD2): Two injections from the same sample. The analyses of LD1 and LD2 give a measure of the precision associated with the laboratory procedure.

3.4 LABORATORY REAGENT BLANK (LRB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the analytical apparatus.

3.5 FIELD BLANK: A PVD sampler left out in the ambient air (for example, attached to a tree) for the duration of the sample-collection period.

3.6 STOCK STANDARD SOLUTION: A concentrated solution containing one or more method analytes prepared in the laboratory by use of using assayed reference materials or purchased from a reputable commercial source.

3.7 WORKING STANDARD SOLUTION: A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.8 SECONDARY STANDARD: A standard from another vender or a different lot number that is used to check the primary standard used for estimating concentrations.

4.0 Health and Safety Warnings

4.1: The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; therefore, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of the Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of data-handling sheets should be made available to all personnel involved in these analyses. Use these reagents in a fume hood whenever possible; and if eye or skin contact occurs, flush with large volumes of water.

4.2: Always wear safety glasses or a shield for eye protection, wear protective clothing, and observe proper mixing when working with these reagents.

Table 2*A*. Typical achievable reporting limits for volatile organic compounds commonly detected in passive-vapor-diffusion samplers from a gas chromatograph equipped with a photoionization detecter and an electron capture detector

Volatile organic compound	Reporting limit, in parts per billion by volume
Benzene	10
Ethylbenzene	50
meta/para-xylenes	50
ortho-xylene	80
Toluene	40
Chlorobenzene	50
Trichloroethylene	10
Tetrachloroethylene	2
1,1-Dichloroethene	10
cis-1,2-Dichloroethene	15
trans-1,2-Dichloroethene	10
1,1,1-Trichloroethane	6

4.3: Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin and eyes.

5.0 Personnel Qualifications

5.1: The analyst should have at least a 4-year degree in a physical science.

5.2: The analyst should be trained at least 1 week and have a working knowledge of this method and quality control before initiating the procedure.

5.3: All personnel shall be responsible for complying with all quality-assurance/quality-control requirements that pertain to their organizational/technical function.

6.0 Equipment and Supplies

6.1: Gas chromatograph equipped with a photoionization detector (PID) in series with an electron capture detector (ECD), and an analytical column capable of separating target analytes.

6.2: Data-collection system (for example, a chart recorder, intergrator or a portable computer).

6.3: Syringes: steel barrel, volume of 250 µL to 500 µL; 2 in., 25-gauge needle.

6.4: Vials: 40 mL volatile organic analysis (VOA) vials with Teflon lined septum caps.

7.0 Preparation of Air and Aqueous Standards

7.1: The air standard for each target analyte is the headspace above a l0 µg/L aqueous standard at approximately 0 to 1°C for each target analyte. Aqueous standards are prepared with target analyte concentrations of 10 µg/L and are stored on ice in 40 mL VOA vials with no head space. When ready for use, 10mL of the aqueous standard are withdrawn from the vials to produce a headspace from which vapors are analyzed and serve as air standards. The vials are then placed into an ice bath in a cooler with the septa side facing downward, and left to equilibrate for approximately 30 minutes. Because the concentration of the volatile organic compounds in the head space was calibrated at approximately 0 to l°C, the working standards must be maintained at the same temperature.Vapor-standard concentrations of volatile organic compounds commonly detected with passive-vapor-diffusion samplers in the headspace of a 10 µg/L aqueous standard at approximately 0 to l°C have been determined through in-house experimentation and are shown in table 2*B*.

Table 2*B*. Vapor concentrations of volatile organic compounds commonly detected with passive-vapor-diffusion samplers in the head space of a 10 micrograms per liter aqueous standard at approximately 0 to 1 degree Celsius

Volatile organic compound	Concentration, in parts per billion by volume
Benzene	151
Ethylbenzene	145
meta/para-xylenes	136
ortho-xylene	112
Toluene	159
Chlorobenzene	70
Trichloroethylene	142
Tetrachloroethylene	201
1,1-Dichloroethene	554
cis-1,2-Dichloroethene	90
trans-1,2-Dichloroethene	202
1,1,1-Trichloroethane	330

7.2: Aqueous standards are made weekly from a methanol stock solution and volatile organic-free water, and stored in a 40-mL VOA vial on ice with no head space.

7.3: The methanol stock standard and secondary stock standard are replaced every 3 months.

7.4: The aqueous working and secondary standards are good for 7 days provided these standards are stored on ice with no headspace.

8.0 Instrument Operation

Gas chromatographs are available from many commercial sources. Operation of any particular gas chromatograph should be in accordance with procedures supplied by the manufacturer.

9.0 Instrument Calibration

Calibration for analysis of vapor samples collected with PVD samplers generally consists of taking a 200 µL volume of the headspace in the 10 µg/L aqueous, 0 to 1°C standard with a 250 µL steel-barrel syringe with a 2 in., 25-gauge needle, and injecting it into the injection port of the GC. The actual vapor concentration is listed in table 2*B* for selected compounds. This single point calibration is completed by analyzing a blank, which is obtained from the headspace above a volatile organic-free water sample in a 40 mL VOA vial.

10.0 Analysis

10.1: Insert the syringe needle into the PVD-sampler septum and use the plunger to flush the syringe barrel three times. After flushing, pull the plunger up to the 200 µL point on the barrel and remove the needle from PVD sample.

10.2: Insert the syringe needle into the GC injection port, and push the needle through the septum until the barrel comes up against the injection port, immediately push the plunger with a quick action, remove needle from injection port, and turn on the data-collection system.

10.3: Record the following information:

1. start of run,
2. sample number,
3. sample volume,
4. attenuation or gain, and
5. other relevant comments.

10.4: The order in which of a group of samples is analyzed is as follows:

10.4.1: Calibration Standard—Inject a 200-µL sample of 10-µg/L standard at 0 to 1°C headspace into the GC. Keep standard peaks at approximately 50 percent scale or more, if possible, by adjusting the attenuation or gain.

10.4.2: Repeat 10-µg/L standard to check for reproducibility. Standard chromatograms should have compound peak heights within 15 percent of each other and retention times should be identical.

10.4.3: Inject the secondary standard for confirmation. The acceptance criteria is within 20 percent of the true value.

10.4.4: Clean air blank—Inject a 200-µL sample of clean air into the gas chromatograph with the attenuation set at the same level or lower than the level at which samples will be run. Blank clean air is taken from the headspace above volatile organic-free water in a 40-mL VOA vial.

10.4.5: Samples—Inject 200-µL sample volume into the GC at the same attenuation level at, or lower than the attenuation at which the standard was run. If contaminant levels on the chromatograms are off-scale, adjust the attenuation or gain to decrease instrument response. If the chromatographic peaks are still off-scale, rerun the samples with a smaller injection volume.

10.4.6: Repeat 10-µg/L calibration standard every 10 samples and at the end of the sample batch to check the calibration and reproducibility. Standard chromatograms should have compound peak heights within 20 percent of each other, and retention times should be identical.

11.0 Identification and Estimated Concentration

11.1: Identify compounds present in a sample by matching retention times of peaks in the sample chromatogram to the retention times of standard peaks determined at site.

11.2: Concentrations are estimated by a peak-height or peak-area comparison. For example, if the l0-µg/L aqueous-standard head space had a benzene peak height of 32 units from a 200-µL injection with instrument attenuation at 2, an identified benzene peak l2 units high from a 200-µL sample injection with instrument attenuation at 2 would represent a sample benzene concentration of 57 ppb v.

$$\frac{32 \text{ units}}{*151 \text{ ppb v}} = \frac{12 \text{ units}}{X \text{ ppb v}}$$

$$X = 57 \text{ ppb v Benzene}$$

* See Air Standard Section 7.1 (table 2*B*)

12.0 Interferences

12.1: Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample-processing hardware that lead to discrete artifacts and (or) elevated baselines in the chromatograms. All of these materials must routinely be demonstrated to be free from interferences under the conditions of the analysis by running laboratory and field method blanks.

12.2: Matrix interferences may be caused by contaminants that coelude with the target compounds. The extent of matrix interferences will vary considerably from source to source. A different column or detector may eliminate this interference.

12.3: Contamination by carry-over can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carry-over, a VOA free water blank should be analyzed following an unusually concentrated sample to assure that the syringe is clean.

13.0 Quality Control

Quality-control procedures and acceptance criteria listed below, along with corrective actions, are shown in table 2*C*.

13.1: A blank and a 1-point standard is used for instrument calibration. Initially, run a 10-µg/L standard (at 0–1°C) to determine retention times and response

Table 2*C*. Quality controls, acceptance criteria, and corrective actions

[DQO, data-quality objective; RL, reporting limit; RPD, relative percent difference; <, less than]

Quality-control item	Frequency	Acceptance criteria	Corrective action
Initial calibration	Daily, before samples	< 15 percent difference from the first standard[1]	Inject another standard, check system
Blank	Daily, every batch	< 1/2 of RL[1]	Repeat blank injection, prepare a new blank, check system, increase RLs depending on DQOs
Second source standard	Daily, every batch	< 20 percent difference from true value[1]	Inject another standard, repeat initial calibration, check system
Continuing calibration	Every 10 samples and after the last sample	< 20 percent difference from previous standard[1]	Inject another standard, repeat initial calibration, check system
Field duplicate	Every 20 samples	< 30 percent RPD[1]	Repeat injection
Laboratory duplicate	Daily, every 20 samples	< 20 percent RPD[1]	Repeat injection, run another duplicate
Field blank	At least one per survey	<1/2 of RL[1]	Repeat injection. Evaluate data using technical judgement

[1]Acceptance criteria defined by technical judgement.

factors of instrument. Repeat the 10-µg/L standard to check the reproducibility. Acceptance criteria for this initial calibration is less than 15 percent difference from the first standard injection.

13.2: Laboratory blanks are analyzed at the initial calibration and periodically to be sure of no carry over from previous injections. Technical judgement is used to determine frequency of blank-sample analysis. Acceptance criteria is no target-compound peaks greater than one-half the reporting level.

13.3: A second source standard containing some compounds of interest is analyzed daily to verify calibration standard. Acceptance criteria is less than 20 percent difference of the true value.

13.4: A standard is run at least every 10 samples and at the end of the sample batch to update the instrument calibration. Acceptance criteria is less than 20 percent difference from previous standard.

13.5: Run field and laboratory duplicates every twenty samples. Acceptance criteria is a relative percent difference between the two values of less than 30 percent for field duplicates and 20 percent for laboratory duplicates.

13.6: Field blanks are analyzed at least once per survey. Field blanks are PVD samplers left out in ambient air (for example, attached to a tree) for the duration of the sample-collection period and are retrieved and analyzed the same day(s) as samples. Acceptance criteria is no target-compound peaks greater than one-half the reporting level.

14.0 Data and Records Management

14.1: All work performed for the analyses of samples must be entered into a field logbook. These data are then reviewed and verified for precision, accuracy, and representativeness by the project chief or project manager with analysis of the quality-assurance data.

14.2: The samples analyzed are logged into a laboratory-information-management system.

14.3: Chromatograms generated are saved and filed in a project folder.