

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

# Assessment of Volatile Organic Compounds in Surface Water at Canal Creek, Aberdeen Proving Ground, Maryland November 1999–September 2000

Open-File Report 01-292

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# U.S. Department of the Interior GALE A. NORTON, SecretaryU.S. Geological Survey Charles G. Groat, Director

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# **Conversion Factors and Vertical Datum**

Multiply	Ву	To obtain
inch (in.)	2.54	centimeter
foot (ft)	0.3048	meter
square foot (ft <sup>2</sup> )	0.0929	square meter
foot per day (ft/d)	0.3048	meter per day
cubic foot per second (ft <sup>3</sup> /s)	0.02832	cubic meter per second
mile (mi)	1.609	kilometer
square mile (mi <sup>2</sup> )	2.590	square kilometer

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

Other abbreviated units of measure: Water temperature, chemical concentration, and other chemical and physical properties of constituents are given in metric units.

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

$$^{\circ}F = (1.8 \times ^{\circ}C) + 32$$

Chemical concentration in water is expressed in milligrams per liter (mg/L) and micrograms per liter (µg/L).

# **Abbreviations:**

The following volatile organic compounds (VOCs) are abbreviated in this report:

Carbon tetrachloride (CT)	Chloroform (CF)
1,2-dichloroethene (DCE)	1,2-dichloroethane (DCA)
1,1,2,2-Tetrachloroethane (TeCA)	Tetrachloroethene (PCE)
Trichloroethene (TCE)	Vinyl chloride (VC)

# Assessment of Volatile Organic Compounds in Surface Water at Canal Creek, Aberdeen Proving Ground, Maryland, November 1999–September 2000

By Daniel J. Phelan, Lisa D. Olsen, Michael P. Senus, and Tracey A. Spencer

# **Abstract**

The purpose of this report is to describe the occurrence and distribution of volatile organic compounds in surface-water samples collected by the U.S. Geological Survey in the Canal Creek area of Aberdeen Proving Ground, Maryland, from November 1999 through September 2000. The report describes the differences between years with below normal and normal precipitation, the effects of seasons, tide stages, and location on volatile organic compound concentrations in surface water, and provides estimates of volatile organic concentration loads to the tidal Gunpowder River. Eighty-four environmental samples from 20 surface-water sites were analyzed. As many as 13 different volatile organic compounds were detected in the samples. Concentrations of volatile organic compounds in surface-water samples ranged from below the reporting limit of 0.5 micrograms per liter to a maximum of 50.2 micrograms per liter for chloroform.

Chloroform was detected most frequently, and was found in 55 percent of the environmental samples that were analyzed for volatile organic compounds (46 of 84 samples). Carbon tetrachloride was detected in 56 percent of the surface-water samples in the tidal part of the creek (34 of 61 samples), but was only detected in 3 of 23 samples in the nontidal part of the creek. 1,1,2,2-Tetrachloroethane was detected in 43 percent of the tidal samples (26 of 61 samples), but was detected at only two nontidal sites and only during November 1999. Three samples were collected from the tidal Gunpowder River about 300 feet from the mouth of Canal Creek in May 2000, and none of the samples contained volatile organic compound concentrations above detection levels. Volatile organic compound concentrations in surface water were highest in the reaches of the creek adjacent to the areas with the highest known levels of ground-water contamination. The load of total volatile organic compounds from Canal Creek to the Gunpowder River is approximately 1.85 pounds per day (0.84 kilograms per day), or 674 pounds per year. Volatile organic compounds that reach the Gunpowder River become substantially diluted. Although natural-attenuation processes in the study area such as biodegradation are highly effective at reducing contaminant concentration in ground water before it discharges to the creek, natural attenuation is not 100 percent effective at all locations or under all tidal, seasonal, and climatic conditions as indicated by detection of volatile organic compounds in Canal Creek.

# Introduction

Since 1917, Aberdeen Proving Ground (APG), Maryland, has been primarily a weapons, ordnance, and chemical-warfare research and development center for the U.S. Army (fig. 1). Most of APG's chemical-manufacturing and munitions-filling plants were located in the area between the West Branch and East Branch of Canal Creek (fig. 2). After World War II, large-scale production and filling operations declined sharply, and many of the plants have since been demolished or abandoned.

Organic solvents, such as carbon tetrachloride (CT), 1,1,2,2-tetrachloroethane (TeCA), and trichloroethene (TCE) were probably the most common wastes produced in large quantities from the manufacturing, filling, and other miscellaneous activities in the Canal Creek area. All of the major manufacturing plants, except for the chlorine plants, used solvents as raw materials, decontaminating agents, or cleaning agents (Nemeth, 1989; Lorah and Clark, 1996). Waste from many of these activities was discharged into the East and West Branch Canal Creek either directly through overland runoff, sewer discharges, or burial, or indirectly through the discharge of contaminated ground water into the wetland areas.

In the late 1960s, potentially contaminated construction materials from the demolition of some manufacturing plants were pushed out into the Canal Creek wetland, creating landfills where there were originally natural wetland sediments (Oliveros and Vroblesky, 1989; Lorah and Clark, 1996). These disposal activities further contributed to contamination of the Canal Creek aquifer in the study area (Lorah and Clark, 1996). None of the manufacturing or other sources of ground-water contamination have been active since the 1970s, along the West Branch Canal Creek south of Hanlon Road (fig. 3).

The term "natural attenuation" refers to naturally occurring processes in soil and ground-water environments that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentrations of contaminants. These in-situ processes include biodegradation, dispersion, dilution, adsorption, volatilization, and chemical or biological stabilization or destruction of contaminants (Wiedemeier and others, 1998). Biodegradation is an important natural-attenuation mechanism in the wetland sediments in the Canal Creek area for reducing the amount of chlorinated hydrocarbons discharging from the contaminated ground water toward the creek (Lorah and others, 1997). Sampling for volatile organic compounds (VOCs) in surface water can aid in determining locations where biodegradation and other natural-attenuation processes are not 100 percent effective at removing contaminants in ground water to below detection limits before they discharge to the creek.

#### **Purpose and Scope**

The purpose of this report is to describe the occurrence and distribution of VOCs in surface-water samples collected by the U.S. Geological Survey in the Canal Creek area from November 1999 through September 2000. The report presents inorganic data, organic data, and an evaluation of the quality-assurance data for the VOCs. The report describes the differences between years with below normal and normal precipitation, the effects of seasons, tide stages, and location on VOC concentrations in the surface water, and provides estimates of VOC loads to the tidal Gunpowder River. Data from Olsen and Spencer (2000) are used in combination with data from this investigation to determine the occurrence and distribution of VOCs between 1999 and 2000.

An estimate of VOC loads to the tidal Gunpowder River is described. Inorganic surface-water quality data from May 2000 are also included to define surface-water characteristics, but are generally not a factor in the interpretation of the VOC data.

#### **Previous Investigations**

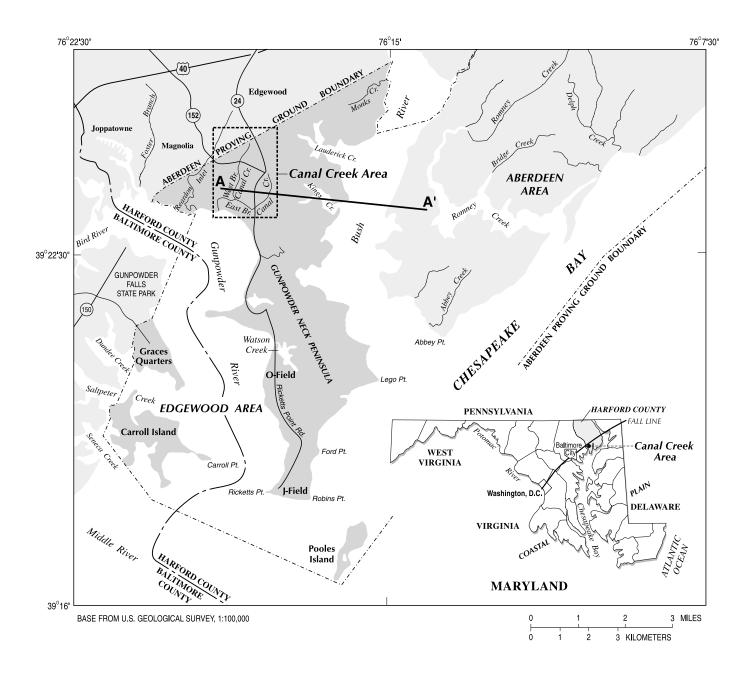
During 1977–78, the U.S. Army Toxic and Hazardous Materials Agency performed the first survey of the soil, sediment, ground water, and surface water of the Edgewood area of APG (Nemeth and others, 1983). The reports by Nemeth (1989) and Lorah and Clark (1996) give the most detailed descriptions of the history and locations of major manufacturing facilities and disposal activities in the Canal Creek area.

A study begun by the USGS in 1985 described the hydrogeology of the site, and determined that a large ground-water contaminant plume was present in a shallow sand aquifer along the West Branch Canal Creek (Lorah and Clark, 1996). Major contaminants in the ground water included the chlorinated VOCs TeCA<sup>1</sup>, TCE, and CT, which are common industrial solvents (Lorah and Clark, 1996).

During September 1988 and June 1989, surface-water samples were collected and analyzed for VOCs, and the results were presented in Lorah and Clark (1996, p. 179 and 180). During the 1988–89 surface-water sampling, all VOC concentrations in the surface-water samples were below the toxicity criteria for freshwater and saltwater aquatic life (U.S. Environmental Protection Agency, 1986).

From 1992 through 1996, the USGS conducted an investigation of the effects of natural attenuation of organic compounds in ground water moving from the Canal Creek aquifer through the fine-grained wetland sediments (Lorah and others, 1997). This study showed that biodegradation and sorption are important mechanisms for natural attenuation of chlorinated hydrocarbons in the wetland sediments. The relatively thin layers of wetland sediments are critical in reducing contaminant concentrations in ground water before it discharges to the wetland surface and the creek. Hydro-

<sup>1.</sup> Although "PCA" has been used as an abbreviation for 1,1,2,2-tetrachloroethane in other reports, "TeCA" has been gaining wider acceptance with the U.S. Army and the regulators at APG as the more correct term.



**Figure 1.** Location of the Canal Creek area, Aberdeen Proving Ground, Maryland, and hydrogeologic section A-A' (shown in fig. 4).

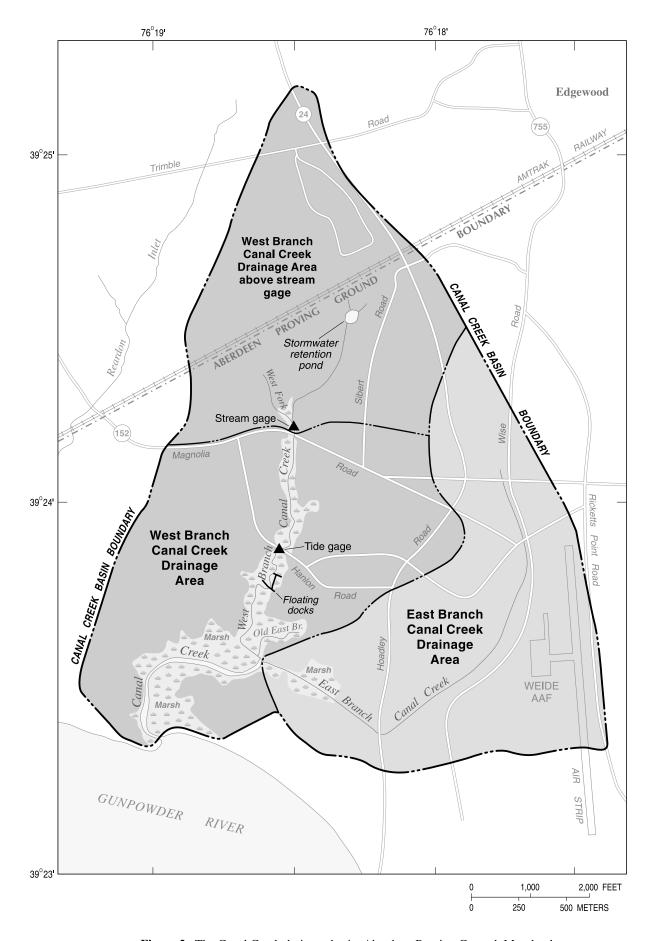


Figure 2. The Canal Creek drainage basin, Aberdeen Proving Ground, Maryland.

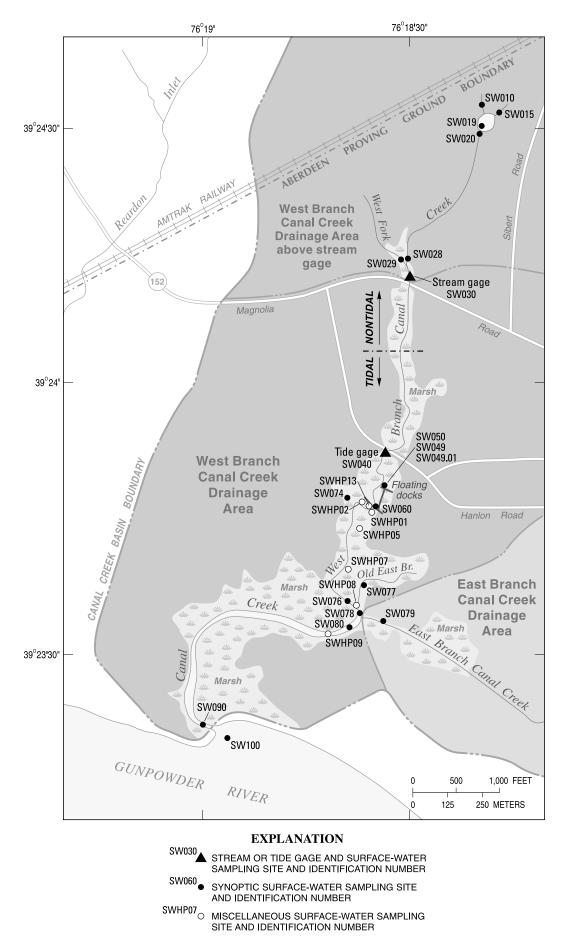


Figure 3. Location of surface-water sampling sites, Canal Creek area, Aberdeen Proving Ground, Maryland.

geologic, water-quality, and sediment-quality data collected by the USGS between 1992 and 1996 in the West Branch Canal Creek area are presented in Olsen and others (1997).

From February through August 1999, the USGS collected surface-water quality data from the West Branch Canal Creek (Olsen and Spencer, 2000). Thirteen surface-water samples from 5 sites were analyzed for VOCs. TeCA was the most frequently detected VOC, and CT and chloroform were found in the highest concentrations. Portions of the data from Olsen and Spencer were included in some statistical calculations used to determine the differences between VOC concentrations in Canal Creek during 1999 and 2000.

From 1997 through 1999, the USGS further defined the importance of natural-attenuation processes on the fate and mobility of VOCs in the wetland and began to characterize the factors that affect biodegradation, such as temperature, location, and initial contaminant concentration. Water-level and water-quality data collected from 1998 through 1999, including VOC data from ground water and surface water, are presented in Spencer and others (2000). Lorah and Olsen (1999a, b) also provide additional evidence of *in-situ* biodegradation in the West Branch Canal Creek wetland.

## **Description of Study Area**

The Canal Creek study area is in the northwest section of the Edgewood Area of APG (fig. 1). The area is a mix of wooded and tidal wetland areas, some open fields, abandoned buildings, office buildings, and warehouses. The Canal Creek drainage area extends beyond the northern boundary of APG into the community of Edgewood, Maryland (fig. 2). When precipitation is heavy, water collects in wooded areas where drainage is poor because of the low permeability of the soils. Land-surface elevations range from a maximum of 150 ft (feet) at the northern edge of the drainage basin in Edgewood, to sea level downstream of Hanlon Road.

Walkways and floating docks were installed by the U.S. Army in 1994 to facilitate access to part of the wetland in the initial West Branch Canal Creek study area (fig. 3). The floating docks consist of a wood frame and cover, and use large rigid foam blocks inside the frame to float each section. Access to part of the wetland beyond the dock area is hindered by tall, dense *Phragmites* grasses, and soft mud that typically is more than 8 ft deep. Surface-water depths can range from 0 to 5 ft, depending on location, tides, and winds (Phelan and others, 2001).

## **Hydrogeologic Setting**

The geology of the Canal Creek area is characterized by thick, wedge-shaped deposits of unconsolidated Coastal Plain sediments that dip southeastward (fig. 4). In the West Branch Canal Creek area, VOCs have been detected in the Canal Creek aquifer. The aquifer ranges from 30 to 70 ft thick in this area (Lorah and Clark, 1996), and is unconfined in the tidal part of the study area. The lower confined aquifer, which underlies the approximately 60-ft-thick lower confining unit, is not known to be contaminated (Lorah and

Vroblesky, 1989; Lorah and Clark, 1996). The upper confining unit, the Canal Creek aquifer, the lower confining unit, and the lower confined aquifer are composed of sediments of the Cretaceous Potomac Group (Oliveros and Vroblesky, 1989).

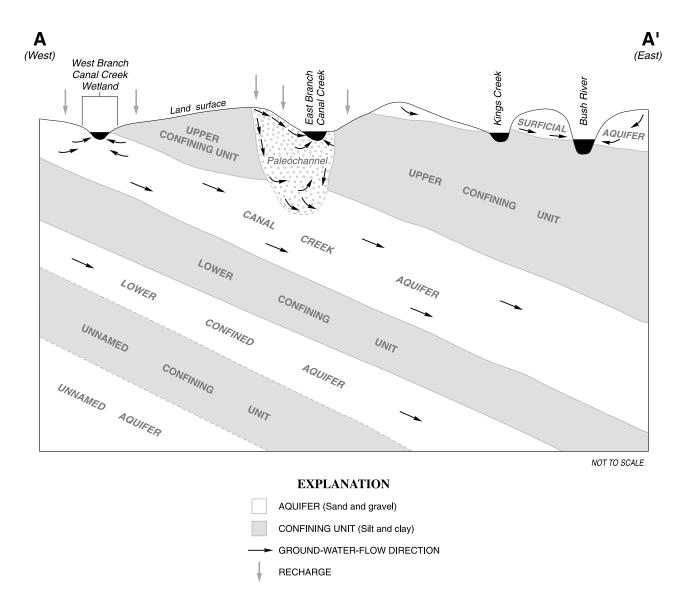
Within the West Branch Canal Creek area, the Canal Creek aquifer sediments consist of medium- to coarse-grained sand and gravel, interfingered with thin layers, or lenses, of clay and silt. East of the wetland, the aquifer is overlain by landfill material and the sediments of the upper confining unit.

Within the wetland area, measurements from previous studies (Lorah and Clark, 1996; Lorah and others, 1997; Phelan and others, 2001), showed that the thickness of the wetland sediments that overlie the Canal Creek aquifer generally ranged from 6 to 25 ft. The wetland sediments typically consist of an upper unit of peat mixed with variable amounts of clay and silt, and a lower unit of silty to sandy clay or clayey sands. Typically, the wetland sediments have a grayish-brown, gray, or black color that is indicative of a reducing environment, although orange or red, narrow oxidized zones are sometimes visible around roots (Lorah and others, 1997). The total organic carbon content of the peat unit ranged from 6.9 to 32 percent, with an average of 18 percent in 15 sediment samples, whereas the total organic carbon content in 4 samples from the lower unit averaged about 1 percent (Olsen and others, 1997).

Ground Water Shallow ground water in the Canal Creek aquifer and the wetland sediments on both sides of West Branch Canal Creek generally flows laterally and upward toward the creek channel. Recharge in the form of precipit-ation occurs upgradient from the creek. Discharge of ground water from the Canal Creek aquifer occurs through the wet-land sediments into the creek and surrounding wetland areas (Lorah and Clark, 1996). The deeper regional ground water flows downgradient toward the southeast (fig. 4).

**Surface Water** The Canal Creek drainage area is approx-imately 2.3 mi<sup>2</sup> (square miles), of which 0.6 mi<sup>2</sup> are up-stream of the stream gage and approximately 0.3 mi<sup>2</sup> are upstream of the APG boundary (fig. 2). The drainage basin for East Branch Canal Creek is 0.8 mi<sup>2</sup>. In contrast, the drainage area for the entire Gunpowder River Basin from the southern tip of the Gunpowder Neck Peninsula into Pennsylvania encompasses approximately 476 mi<sup>2</sup>. Surfacewater samples were collected on the West Branch and East Branch Canal Creek between the APG boundary and the Gunpowder River.

The stream gage was installed on the West Branch Canal Creek at Magnolia Road in August 1999 (fig. 2). A tide gage has been operating on the West Branch Canal Creek at Hanlon Road since 1987 (fig. 2). Graphs showing data from the tide gage and daily rainfall reported by APG from October 1, 1998 through September 30, 2000 are presented in Appendix A.



**Figure 4.** Generalized hydrogeologic section A-A' showing directions of ground-water flow in the Canal Creek area, Aberdeen Proving Ground, Maryland (modified from Lorah and others, 1997, p. 10). [Location of section shown in fig. 1.]

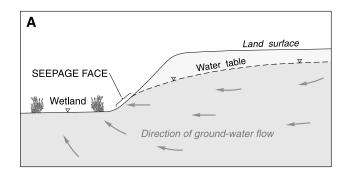
A stormwater retention pond is located on West Branch Canal Creek near the post boundary, along the Amtrak railroad lines (fig. 2). Streamflow is generally toward the south in the Canal Creek Basin. About 30 ft upstream of the stream gage at Magnolia Road, an unnamed tributary hereafter called the "West Fork" discharges to West Branch Canal Creek. A tide gage is located on the West Branch at Hanlon Road at site SW040 (fig. 3). The East Branch discharges into the West Branch, forming the main channel of Canal Creek about 0.63 mi upstream of the confluence of Canal Creek and the tidal Gunpowder River.

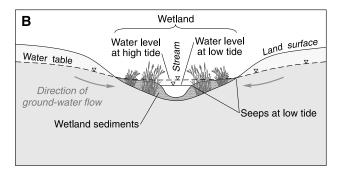
Sources of surface water in the Canal Creek Basin include surface runoff from precipitation, ground-water inflow to the creek channel and wetland, ground-water seeps (springs), and inflow (reverse flow) from the Gunpowder River because of tidal fluctuation. In areas with relatively steep land slopes near the edges of the wetland, the water table may intersect the land surface, resulting in ground-

water discharge directly to the land surface as seeps (fig. 5a). Seeps have been observed in the wetland in areas close to the creek channel at low tide, and in areas close to the marsh boundaries, where ground water discharges directly to surface water without undergoing the natural attenuation processes that occur in the wetland sediments (fig. 5b). The wetland sediments at Canal Creek have been shown to aid the natural attenuation of VOCs as ground water discharges to the creek (Lorah and others, 1997).

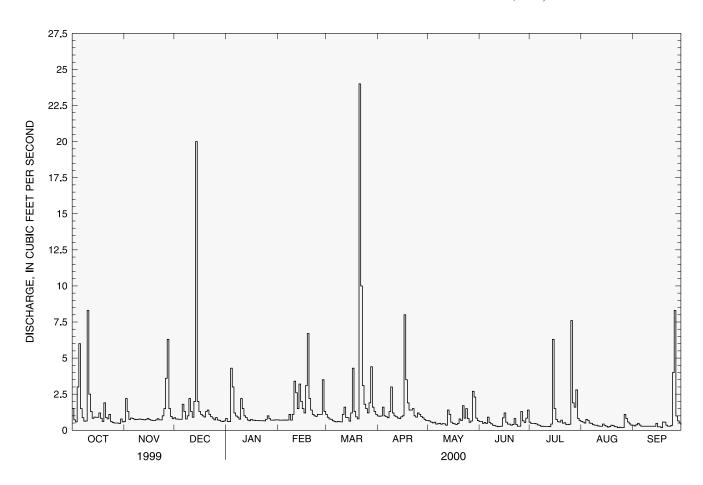
West Branch Canal Creek Discharge at Magnolia Road Gaging Station The discharge from the West Branch Canal Creek is monitored at a USGS stream gage (station number 01585140), on the upstream abutment of the culvert under Magnolia Road (fig. 2). The stream gage was installed in August 1999 to measure the amount and variability of ground-water inflow to the creek upstream of tidal effects, and the variability of base-flow conditions during different seasons. The daily discharge at the gage from October 1999

through September 2000 is shown in figure 6, and the values from the graph and summary statistics are shown in table 1. The annual mean discharge for the period October 1, 1999





**Figure 5.** Areas favorable for formation of seeps at (A) the edge of the wetlands, and (B) at low tide (modified from Winter and others, 1998).



**Figure 6.** Average daily discharge for West Branch Canal Creek at the Magnolia Road stream gage (SW030), October 1999 through September 2000, Aberdeen Proving Ground, Maryland.

Introduction

**Table 1.** Mean daily discharge and summary statistics for the West Branch Canal Creek gaging station at Magnolia Road, Aberdeen Proving Ground, Maryland, October 1999 through September 2000

[Discharge in cubic feet per second; **E**, estimated; MAX, maximum; MIN, minimum; –, not applicable]

DAY	OCT.	NOV.	DEC.	JAN.	FEB.	MAR.	APR.	MAY	JUNE	JULY	AUG.	SEPT.
1	1.50	0.61	0.87	0.82	<b>E</b> 0.72	1.10	0.99	0.68	0.61	0.56	0.61	0.35
2	.72	2.20	.78	.61	<b>E</b> .70	.90	.97	.64	.61	.47	.57	.30
3	.58	1.30	<b>E</b> .77	.60	<b>E</b> .70	.78	.99	.56	.48	.47	.50	.38
4	3.00	.75	<b>E</b> .76	4.30	<b>E</b> .70	.76	1.60	.51	.54	.47	.75	.48
5	6.00	.85	<b>E</b> .76	3.00	<b>E</b> .71	.66	1.00	.56	.47	.44	.69	.36
6	1.50	<b>E</b> .82	1.80	1.20	<b>E</b> .70	.61	.94	.43	.91	.37	.50	.28
7	.87	<b>E</b> .76	1.30	.99	<b>E</b> .71	.58	.87	.45	.53	.34	.48	.28
8	.63	<b>E</b> .74	<b>E</b> .78	.91	<b>E</b> 1.10	.61	1.30	.48	.45	.27	.39	.28
9	.64	<b>E</b> .76	<b>E</b> 1.00	.77	<b>E</b> .70	.59	3.00	.42	.35	.28	.35	.28
10	8.30	<b>E</b> .78	<b>E</b> 2.20	2.20	<b>E</b> 1.10	.58	1.20	.46	.32	.27	.35	.28
11	2.50	<b>E</b> .76	<b>E</b> 1.30	1.50	3.40	1.10	1.00	.44	.28	.27	.30	.28
12	1.30	<b>E</b> .74	<b>E</b> .90	1.00	2.60	1.60	.94	.35	.25	.27	.28	.28
13	.83	<b>E</b> .72	<b>E</b> 2.00	.88	1.50	.88	.85	1.40	.27	.25	.28	.28
14	.91	<b>E</b> .76	<b>E</b> 20	.71	3.20	.87	.81	1.10	.28	.43	.43	.28
15	.90	<b>E</b> .82	<b>E</b> 2.00	.66	2.00	.63	.93	.56	.86	6.30	.34	.48
16	.90	<b>E</b> .74	<b>E</b> 1.30	.75	1.50	1.20	1.00	.48	1.20	1.50	.28	.24
17	1.20	<b>E</b> .70	<b>E</b> 1.10	.70	1.20	4.30	8.00	.44	.56	.74	.22	.24
18	.83	<b>E</b> .68	<b>E</b> 1.00	.69	3.10	1.30	3.50	.40	.43	.59	.26	.18
19	.61	<b>E</b> .68	<b>E</b> .92	.67	6.70	.93	1.90	.47	.42	.57	.35	.57
20	1.90	<b>E</b> .72	<b>E</b> 1.30	<b>E</b> .67	2.20	.79	1.40	.78	.35	.70	.33	.56
21	.88	<b>E</b> .80	1.40	<b>E</b> .66	1.40	24	1.40	.67	.40	.49	.25	.35
22	.79	<b>E</b> .72	1.10	<b>E</b> .66	1.10	10	1.50	1.70	.81	.52	.24	.28
23	1.10	<b>E</b> .72	.94	<b>E</b> .66	1.00	3.10	1.00	.84	.39	.39	.18	.28
24	.61	<b>E</b> 1.00	.84	.65	.96	1.80	.91	1.50	.28	.39	.21	.34
25	.54	1.50	.72	.76	1.10	1.50	1.20	.81	.28	.42	.18	4.0
26	.50	3.60	.88	<b>E</b> 1.00	1.10	1.20	1.10	.55	1.30	7.60	.18	8.30
27	.50	6.30	.71	<b>E</b> .80	1.10	1.90	.95	.64	.66	1.90	1.10	.99
28	.50	1.50	.69	<b>E</b> .70	3.50	4.40	.87	2.70	.54	1.60	.81	.65
29	.47	.96	.63	<b>E</b> .70	1.30	1.60	.75	2.30	.84	2.80	.57	.51
30	.78	.80	.60	<b>E</b> .71	_	1.30	.68	.84	1.40	.82	.44	.36
31	.58	_	.65	<b>E</b> .72	_	1.10	_	.67	_	.68	.35	_

**Table 1.** Mean daily discharge and summary statistics for the West Branch Canal Creek gaging station at Magnolia Road, Aberdeen Proving Ground, Maryland, October 1999 through September 2000—Continued

	OCT.	NOV.	DEC.	JAN.	FEB.	MAR.	APR.	MAY	JUNE	JULY	AUG.	SEPT.
MEAN	1.38	1.16	1.68	1.02	1.65	2.34	1.45	0.80	0.57	1.07	0.41	0.76
MAX	8.30	6.30	20	4.30	6.70	24	8.00	2.70	1.40	7.6	1.10	8.30
MIN	.47	.61	.60	.60	.70	.58	.68	.35	.25	.25	.18	.18

# SUMMARY STATISTICS (cubic feet per second)

Annual Mean	1.19	
Highest Daily Mean	24	Mar. 21, 2000
Lowest Daily Mean	.18	Aug. 23, 25, 26, and Sept. 18, 2000
Annual Seven-Day Minimum	.22	Aug. 20, 2000
Instantaneous Peak Flow	59	Mar. 21, 2000
Instantaneous Low Flow	.18	Aug. 17, 2000
10-percent Exceeds	2.0	
50-percent Exceeds	.74	
90-percent Exceeds	.28	

# **Methods of Investigation**

Surface-water VOC samples were collected at 6 sites in November 1999 and September 2000, at 8 sites in February 2000, and at 20 sites in the May 2000 sampling round (fig. 3). Site identification numbers range from SW010 through SW100. The prefix "SW" in the identification number represents "surface water," and site numbers increase with distance downstream. The lowest numbers, SW010 and SW015, are located farthest upstream at the inflows to the stormwater retention pond (SW019) near the APG boundary. The highest number, SW100, is located in the Gunpowder River. Sites SW010 through SW030 are nontidal sites. Sites SW040 through SW100 are in the tidal part of the creek.

The site numbers and descriptions of each sampling location are listed in table 2. Surface-water samples were collected during base-flow conditions. There was no significant rainfall for at least 3–4 days before each sampling round. In this report, sample names are a combination of the site name from which the sample was collected, followed by the letters H, M, or L. The letters indicate whether the sample was collected at high tide (H), mid tide (M), or low tide (L). The mid-tide samples in this study were always collected as the tide was going out, midway between high and low tides. In addition, seven surface-water samples were collected once from selected hoverprobe drilling sites (Phelan and others, 2001) in March or September 2000 for comparison to ground-water samples that were collected simultaneously at those sites. The hoverprobe surface-water sample sites are not listed in table 2, but the locations are shown in figure 3.

In most cases, samples were collected based on predicted times of tides. Wind direction and speed, precipitation events, ice, and other weather conditions in the Gunpowder River and the Chesapeake Bay area can dramatically affect the water levels in the creek, so the water levels in the tidal part of the creek were not always consistent with the predicted tides.

Field parameters measured at most sites included specific conductance, pH, and water temperature. Specific conductance was measured with a YSI Model 3000 Temperature-Level-Conductivity meter. Calibration of the meter was verified before each sampling round with three conductance standard solutions of approximately 200 μS/cm (microsiemens per centimeter), 500 μS/cm, and 1,000 µS/cm. The meter output was always within 3 percent of each calibration standard. An Orion 290A meter with a gel-filled, temperature-compensated probe was used to measure pH. The pH meter was calibrated before each sampling round with two pH buffers (4 and 7). Meter calibration was also verified with calibration buffers at various times during each sampling round. Water temperature was measured with the Orion 290A pH meter or with the YSI Model 3000 meter.

## **Inorganic Analyses**

The USGS National Water-Quality Laboratory (NWQL) in Denver, Colorado, performed inorganic analyses on five samples that were collected at 2 sites (SW050 and SW060) during the May 2000 sampling effort. The samples were collected using a peristaltic pump with the intake tube inserted into the creek on the upstream side of the floating dock at each site depending on streamflow direction (incoming or outgoing tide). Samples were pumped into bottles with either raw or filtered water (in-line 0.45-micron filter) depending on the sampling protocol. Inorganic samples were chilled immediately after collection and during shipment to NWQL. Samples were analyzed for major ions including calcium, magnesium, sodium, potassium, chloride, sulfate, fluoride, silica, iron, and manganese. Methods used by NWQL for analysis of inorganic constituents in water samples are explained in detail in Fishman and Friedman (1989), and in Fishman (1993).

## **Organic Analyses**

Surface-water samples for VOCs were collected at each site by dipping an 8-mL (milliliter) pre-cleaned sample vial 3 to 5 in. (inches) below the water surface. The vial was then carefully capped while underwater to limit sample aeration and VOC loss because of volatilization or degassing, then placed on ice. VOC samples were collected in triplicate in case of instrument problems during calibration or analyses, or from matrix effects. Some replicates were analyzed to help determine the variability of the collection methods and analytical techniques. Samples from the seep sites were collected by submerging the vials as deep as possible without disturbing the sediments, but in some cases this was only 1 in. or less below the water surface.

VOC samples were placed on ice and carried to the laboratory where they were kept refrigerated prior to analysis. The U.S. Geological Survey Maryland-Delaware-D.C. District Water-Quality Laboratory (referred to as the "on-site laboratory" throughout this report) is located about 1,000 ft southeast of site SW060. Samples were analyzed within 14 days of collection for VOCs using a purge-and-trap capillary gas chromatograph with a mass-selective detector. The analytical method used to analyze for VOCs is equivalent to U.S. Environmental Protection Agency method 524.2 (1985), and is described in Rose and Schroeder (1995). The lower calibration limit for VOC analyses ranged from 0.5 to 5.0  $\mu$ g/L (micrograms per liter). The upper calibration limit for VOC analyses ranged from 200 to 250  $\mu$ g/L.

As part of the on-site laboratory's internal quality assurance and quality control, internal standards and surrogate standards were injected into every blank and environmental sample. Two internal standards of known concentration were used to determine the relative response of each target compound. Concentrations of the target compounds were calculated based on their responses relative to internal standards with the most similar retention times. Three surrogate standards with similar masses and chemical structures to the analytes of interest were used to track possible variations in each analytical sample run. The surrogate concentrations

Table 2. Surface-water sampling sites for the Canal Creek area, Aberdeen Proving Ground, Maryland

[Site locations are shown in figure 3;  $^{\circ}$ , degrees,  $^{\prime}$ , minutes,  $^{\shortparallel}$ , seconds; mi, miles; ft, feet]

Site name	Distance upstream of mouth (mi) <sup>A</sup>	Tidal or nontidal reach	Latitude	Longitude	Site description
SW010	2.09	Nontidal	39 24 33	76 18 21	West Branch Canal Creek at north inlet to the stormwater retention pond.
SW015	2.09	Nontidal	39 24 32	76 18 18	East inlet to the stormwater retention pond.
SW019	2.05	Nontidal	39 24 31	76 18 21	Stormwater retention pond.
SW020	2.04	Nontidal	39 24 29	76 18 21	West Branch Canal Creek 20 ft downstream of the stormwater retention pond.
SW028	1.57	Nontidal	39 24 16	76 18 32	West Branch Canal Creek about 50 ft upstream of stream gage and the confluence with West Fork.
SW029	1.57	Nontidal	39 24 16	76 18 33	West Fork of the West Branch Canal Creek about 50 ft upstream of stream gage.
SW030	1.56	Nontidal	39 24 14	76 18 32	West Branch Canal Creek at the U.S. Geological Survey stream gage at Magnolia Road.
SW040	1.15	Tidal	39 23 53	76 18 35	West Branch Canal Creek at the tide gage at Hanlon Road.
SW049	1.04	Tidal	39 23 48	76 18 35	Surface water near tracer array between piezometers WB35 and WB36 north of walkway.
SW049.01	1.04	Tidal	39 23 48	76 18 35	Seep north of the upstream floating docks occurs during low tide.
SW050	1.05	Tidal	39 23 48	76 18 35	West Branch Canal Creek at end of the upstream floating docks.
SW060	.98	Tidal	39 23 47	76 18 36	West Branch Canal Creek at floating walkbridge of the downstream floating docks near the staff gage.
SW074	.97	Tidal	39 23 48	76 18 40	Unnamed tributary about 120 ft upstream of the West Branch.
SW076	.67	Tidal	39 23 37	76 18 41	West Branch Canal Creek about 120 ft upstream of confluence of the Old East Branch Channel.
SW077	.70	Tidal	39 23 37	76 18 38	Old East Branch channel about 240 ft upstream of the West Branch.
SW078	.63	Tidal	39 23 34	76 18 39	West Branch Canal Creek about 75 ft upstream of confluence with the East Branch.
SW079	.67	Tidal	39 23 33	76 18 36	East Branch Canal Creek about 60–90 ft upstream of confluence with the West Branch.
SW080	.62	Tidal	39 23 33	76 18 40	Canal Creek about 240 ft downstream of confluence of the East and West Branches.
SW090	.02	Tidal	39 23 22	76 19 03	Canal Creek about 150 ft upstream of the confluence with the Gunpowder River.
SW100	05	Tidal	39 23 20	76 18 59	Gunpowder River about 300 ft from the mouth of Canal Creek.

A. Distance upstream of mouth measured along the creek channel. Negative value indicates distance is downstream of mouth.

were known values; therefore, the responses of the surrogates could be evaluated to detect variations in instrument performance. If a sample was processed and either the internal standard responses were low or any of the surrogate responses were more than 30 percent higher or lower than the expected concentration, then a replicate was analyzed and, if necessary, the instrument was adjusted and recalibrated before other samples were analyzed.

# **Water-Quality Data**

The following sections present the results of the inorganic and organic surface-water-quality data collected at Canal Creek, and the evaluation of the quality-assurance data collected for the VOC data. Evaluation of the quality of the surface-water data is an important step in data interpretation. In this report, data quality is assessed in relation to two types of error—bias and variability.

## **Inorganic Water-Quality Data**

Five surface-water samples were collected and analyzed during the May 2000 sampling round to determine the differences in major-ion concentrations during one tide cycle. Samples were collected during high, mid, and low tides at site SW050, and during high and low tides at site SW060 (fig. 3). These sites are located where the two floating docks in the original study area intersect the creek channel. The results of these analyses are presented in table 3. These analyses are typical of this specific tidal cycle, and do not reflect seasonal or annual variation.

During high tides, the specific conductance and concentrations of magnesium, sodium, potassium, chloride, sulfate, and bromide all increased in comparison to the low and outgoing mid-tide samples, indicating that the primary source of these ions was from the Gunpowder River and Chesapeake Bay.

Concentrations of silica, iron, manganese, nitrate plus nitrite, and ammonia were higher during low tide than during high tide. This result indicates that these ions were discharging from the basin and ground water in concentrations higher than those normally found in the Gunpowder River. This result is indicative of the normal exchange of major ions in areas where fresh surface water mixes with brackish tidal waters.

#### **Organic Water-Quality Data**

The VOC data for surface-water samples are presented in Appendix B. The field parameters that were analyzed (specific conductance, pH, and temperature) are also listed.

In addition to data from the four synoptic surface-water sampling rounds, VOC data from 7 sites that were sampled on a one-time basis outside of these sampling rounds are also included in Appendix B. These samples were collected during the hoverprobe drilling and ground-water profiling program and during subsequent ground-water sampling at the hoverprobe sites during 2000 (Phelan and others, 2001).

Surface-water VOC data from the March 2000 hoverprobe sites (SWHP07, SWHP08, and SWHP09) were used along with data from Olsen and Spencer (2000) in calculating VOC loads to the Gunpowder River, but were not used in any other interpretations in this report because they were not collected in conjunction with other synoptic sampling rounds.

The 13 VOCs presented in Appendix B are the only compounds for which there were any concentrations above the lower detection limit (0.5  $\mu$ g/L–5.0  $\mu$ g/L). Forty-six compounds were analyzed for but not detected in any environmental or quality-assurance sample above the lower detection limit. Those compounds are listed in table 4.

One-hundred thirty-five sample analyses are listed in Appendix B. Eighty-four environmental samples were analyzed for VOCs, not counting duplicate, triplicate, or quality-assurance samples. These analyses include 32 duplicate pairs and one triplicate set, and 11 blanks of various types.

The VOCs in Appendix B are listed with heavier, more chlorinated, compounds preceding the lighter ones, so that the chlorinated ethanes appear first, starting with 1,1,2,2-tetrachloroethane, followed by 1,1,2-trichloroethane, and so on, ending with 1,2-dichloroethane. The chlorinated ethenes are listed next, starting with tetrachloroethene and ending with vinyl chloride, and are followed by the chlorinated methanes, carbon tetrachloride and chloroform. The remaining VOCs of lesser interest are listed after the groups of chlorinated solvents.

Reporting limits varied between 0.5 and 5.0  $\mu$ g/L, depending on the compound and date of analysis, because of matrix interferences and periodic variations in instrument performance. Reporting limits were determined and verified through repeated analyses of calibration standards. Concentrations were rounded to the nearest 0.1  $\mu$ g/L.

Quality Assurance of Volatile Organic Compound
Data Quality-assurance samples were collected to evaluate
bias and variability in VOC concentration data. Bias is
system-atic error that may result from contaminants being
intro-duced into a sample or analytes being lost from a
sample during collection, processing, or analysis. Variability
is ran-dom error in independent measurements of the same
quan-tity, and may result from variations in sampling or
analytical procedures. For environmental samples and their
replicates, intrinsic heterogeneities in the quantity being
measured (in this case, VOCs in surface water) are also a
source of vari-ability.

Laboratory quality-assurance practices, including the use of laboratory blanks, analytical standards, and surrogate recoveries to assess bias and variability associated with sample analysis, are equivalent to U.S. Environmental Protection Agency method 524.2, given in Rose and Schroeder (1995). All of the surface-water VOC data presented in this report passed the control limits that are documented in the laboratory analytical method in Rose and Schroeder (1995).

Bias and variability also were evaluated by use of field blanks and field replicates. Field blanks and field replicates

**Table 3**. Inorganic surface-water-quality data from West Branch Canal Creek, Aberdeen Proving Ground, Maryland, May 17, 2000

 $[L, low\ tide;\ M, mid\ tide;\ H, high\ tide\ in\ sample\ names;\ \mu S/cm,\ microsiemens\ per\ centimeter;\ ^{\circ}C,\ degrees\ Celsius;\ mg/L,\ milligrams\ per\ liter;\ <,\ less\ than]$ 

Sample name	Date	Time	Specific conductance, field (µS/cm)	Specific conductance, laboratory (µS/cm)	pH, field, (standard units)	Water temperature (°C)	Calcium, dissolved (mg/L as Ca)	Magnesium, dissolved (mg/L as Mg)	Sodium, dissolved (mg/L as Na)	Potassium, dissolved (mg/L as K)
SW050L	05/17/2000	1535	520	528	7.2	25.1	16.3	11.0	61.9	4.34
SW050M	05/17/2000	1145	675	668	7.5	21.1	16.5	13.2	80.6	5.34
SW050H	05/17/2000	905	722	719	7.6	20.6	15.7	14.5	91.7	6.16
SW060L	05/17/2000	1514	531	515	7.3	25.1	16.2	10.8	59.0	4.12
SW060H	05/17/2000	840	730	724	7.7	20.3	15.6	14.5	91.1	6.17
Sample name	Sulfate, dissolved (mg/L as SO <sub>4</sub> )	Chloride, dissolved (mg/L as Cl)	Fluoride, dissolved (mg/L as F)	Bromide, dissolved (mg/L as Br)	Silica, dissolved (mg/L as SiO <sub>2</sub> )	Nitrogen, nitrate plus nitrite, dissolved (mg/L as N)	Nitrogen, ammonia plus organic (mg/L as N)	Phosphorus, ortho- phosphate (mg/L as P)	Iron, dissolved (mg/L as Fe)	Manganese, dissolved (mg/L as Mn)
SW050L	22.0	107	0.157	0.065	5.80	0.06	0.471	0.01	0.208	0.116
SW050M	26.6	148	.141	.187	4.41	< .05	.424	< .01	.100	.112
SW050H	30.5	164	.126	.321	2.91	< .05	.311	< .01	.043	.036
SW060L	21.7	104	.155	.068	5.90	.07	.463	< .01	.306	.148
SW060H	30.4	163	.169	.320	2.78	< .05	.287	< .01	.029	.029

**Table 4**. Organic compounds that were analyzed for, but not detected in any surface-water sample during the November 1999, and February, May, or September 2000 sampling rounds, Canal Creek area, Aberdeen Proving Ground, Maryland

Benzene	Bromobenzene	Bromochloromethane
Bromoform	Bromomethane	n-Butylbenzene
sec-Butylbenzene	tert-Butylbenzene	2-Chlorotoluene
4-Chlorotoluene	Chlorobenzene	Chloroethane
Chloromethane	Dibromochloromethane	1,2-Dibromo-3-chloropropane
1,2-Dibromoethane	Dibromomethane	1,2-Dichlorobenzene
1,3-Dichlorobenzene	1,4-Dichlorobenzene	1,1-Dichloroethane
1,1-Dichloroethene	1,2-Dichloropropane	1,3-Dichloropropane
2,2-Dichloropropane	1,1-Dichloropropene	cis-1,3-Dichloropropene
trans-1,3-Dichloropropene	Ethyl benzene	Hexachlorobutadiene
Isopropylbenzene	<i>p</i> -Isopropyltoluene	Methylene chloride
Naphthalene	<i>n</i> -Propylbenzene	Styrene
1,1,1,2-Tetrachloroethane	1,2,3-Trichlorobenzene	1,2,4-Trichlorobenzene
1,1,1-Trichloroethane	Trichlorofluoromethane	1,2,3-Trichloropropane
1,2,4-Trimethylbenzene	1,3,5-Trimethylbenzene	<i>m</i> , <i>p</i> -Xylenes
o-Xylene		

integrated sources of bias and variability from all steps of the sample collection, processing, and analysis procedures.

The results of field blanks and trip blanks showed no measurable sample bias in the analytical methods because of field operations or sample handling. Field replicates and matrix spikes showed an acceptable level of variability and reproducibility among theoretically identical samples, even when considering the inherently heterogeneous surfacewater characteristics of the tidal creek.

Field Blanks—Field blanks are typically collected by passing organic-free water through the equipment that is used to collect environmental samples. In this case, the only equipment used to collect the surface-water samples were the sample vials. The sources of contamination bias were therefore limited to the handling procedures and the sample vial itself. Seven field blanks were collected for analysis of VOCs during the May 2000 sampling round to evaluate the potential contamination bias in the surface-water sampling techniques. These field blanks were collected by filling the sample vials in the field with organic-free water and then quickly capping the vials. Two of the seven field blanks were collected by filling the vials while sitting in the motorboat. Two of the seven field blanks were filled at site

SW029, which was accessed by the field vehicle and by foot. Two of the seven field blanks were filled while standing on the floating walkways at site SW060. The field blanks were immediately chilled and carried by hand with the rest of the environmental samples to the on-site laboratory. No VOCs were detected in these blanks; therefore, contaminant bias in the surface-water samples is considered to be negligible. Blanks were not collected during other sampling rounds because there was no reasonable suspicion of contamination due to sampling procedures.

Trip Blanks—Trip blanks are samples of organic-free water in clean VOC vials that were filled before sampling, and carried into the field to determine if any contamination was caused by transportation of samples to and from the field sites. Two trip blanks were used during both the February 2000 and the May 2000 sampling rounds. One of the trip blanks during the May sampling was carried in the van, and then carried by foot to the upstream sites with the rest of the environmental samples. The other trip blank was carried in the motorboat used for sampling the most downstream sites. Both pairs of trip blanks had no detections of organic compounds, indicating no sample bias because of transportation of the sample vials to or from the field.

Field Replicates—Replicate samples collected sequentially at selected sites and sampling times were used to assess the overall variability in the sampling and analytical procedures. The first replicate sample collected for a particular location and time is designated by a "1" and the second sample, or replicate, collected immediately after the first sample, is designated by a "2" in the "Replicate" column in Appendix B. One triplicate was analyzed, and the samples are designated "1, 2, and 3" in the "Replicate" column in Appendix B, and all values for the tripicate samples were non-detects. Variability between replicate samples was determined by calculating the relative percent difference (RPD) of the concentrations of each analyte that was detected in both samples. RPDs were calculated prior to rounding the concentration data, using the absolute value result of the equation,

RPD = 
$$\frac{C_1 - C_2}{(C_1 + C_2)/2} \times 100$$
 percent

where

RPD = relative percent difference,

 $C_1$  = concentration of the first sample, and

 $C_2$  = concentration of the duplicate sample.

The RPDs for replicate analyses of VOCs in surface-water samples are presented in table 5. Reproducibility of the surface-water samples is good based on the average range of RPD values (less than 20 percent). RPDs averaged 12.7 percent, with a minimum of 0.4 percent and a maximum of 81 percent. By comparison, the average RPD for ground-water samples collected by the USGS in the West Branch Canal Creek study area and analyzed at the same on-site laboratory from 1992 to 1996 was 14.6 percent (Olsen and others, 1997). Thirteen duplicate pairs and one triplicate set had non-detects for all compounds in each sample.

One duplicate sample, from site SW049 on September 14, 2000, is not included in table 5 for the following reasons. Site SW049 is immediately adjacent to the floating docks in the wetland study area, and showed very different VOC concentrations between duplicates, particularly for vinyl chloride (VC), and dichlorodifluoromethane (CFC-12) on September 14, 2000 (Appendix B). Sample SW049L, replicate 2, had the only detections of VC  $(33.3 \mu g/L)$  and CFC-12  $(9.8 \mu g/L)$  in the study, whereas the duplicate sample had concentrations below the detection limit for both compounds. The replicate 2 sample was likely from water that was trapped under the docks before sampling, and released under the shifting weight of people walking on the docks; the replicate 1 sample is more representative of the surface water in the area. VC is a compound that results from the eventual degradation of the organic compounds found in the Canal Creek aquifer and the

wetland sediments. In the replicate 2 sample, the high VC concentration represents water that was trapped under the docks, causing build-up of concentrations that are not representative of concentrations elsewhere.

The CFC-12 that was detected in replicate 2 is typically used as an aerosol propellant and refrigerant, and was likely used as a blowing agent in the rigid foam that is used to make the docks float. Kjeldsen and Jensen (2001) described the release of CFCs from polyurethane foam insulation from which CFCs were used as blowing agents. The detections of CFC-12 in the surface water were probably caused only by the rigid foam, and not environmental contamination. CFC-12 is not a likely military contaminant and has not been detected in water from the Canal Creek aquifer. Concentrations of *cis*- and *trans*-1,2-dichloroethene (DCE) were also higher in replicate 2 than in replicate 1. These two compounds are known breakdown (daughter) compounds of VOCs that are found in the aquifer and wetland sediments, and, as with VC, probably became concentrated under the docks.

Matrix Spikes—Matrix spike samples are environmental samples to which known quantities of five organic compounds are added to measure the accuracy of the analytical procedure in detecting the spiked compounds in the particular sample matrix. These samples are also used to determine the changes in analyte concentrations during sample processing and analysis. Matrix-spike duplicates were used to determine the reproducibility of these procedures. Analyses of paired spiked and unspiked samples enable calculation of the spike recovery for each sample, thereby providing a measure of the recovery efficiency for the analytical method and evaluation of matrix effects. Spike recovery, in percent, was calculated using the equation:

Spike recovery in percent = 
$$\frac{Mspiked - Munspiked}{Espiked} \times 100$$
 percent

where

Mspiked = the concentration of the spiked compound **measured** in the spiked sample,

Munspiked = the concentration of the unspiked compound **measured** in the unspiked

sample, and

Espiked = the concentration of the spiked compound expected in the spiked sample based on the volume and concentration of spike

mixture used.

**Table 5.** Relative percent differences for duplicate surface-water organic constituents with concentrations above detection limits, November 1999 through September 2000, Canal Creek, Aberdeen Proving Ground, Maryland

[RPD, relative percent difference; duplicate sample pair SW049 from September 14, 2000 is not included because it was determined that the water in the duplicates was from two different sources. Thirteen duplicate pairs and one triplicate set had non-detects for all compounds in each sample]

Compounds detected	Number of replicate pairs with detections in both samples (out of a total of 31 pairs)	Number of pairs with detection in one sample, but not in the corresponding duplicate	Minimum (percent)	Maximum (percent)	Mean (percent)		
1,1,2,2-Tetrachloroethane	12	0	1.7	81	17.4		
Tetrachloroethene	3	0	4.2	14.7	8.4		
Trichloroethene	4	2	6.2	9.5	8.3		
Carbon tetrachloride	11	3	2.5	26.2	14.4		
Chloroform	14	1	0.4	27.1	9.4		
Overall sample-weighted average of RPDs							

For all matrix spikes analyzed, the calculated recoveries for the five organic spike compounds were within the control limits specified below by the analytical methods (U.S. Environmental Protection Agency, 1985; Rose and Schroeder, 1995):

Selected compound	Percent recovery control limits		
Benzene	76–127		
Chlorobenzene	75–130		
1,1-Dichloroethene	61–145		
Toluene	76–120		
Trichloroethene	71–120		

The minimum percent recovery of the spike compounds in the two matrix spikes and two matrix spike duplicates was 94.5 percent, and the maximum was 128 percent (1,1-di-chloroethene), both within the data-quality objectives for the respective compound. The RPDs for each of the spike compounds in the two sets of matrix spikes and matrix spike duplicates ranged from 0 to 24.4 percent, which is within the control limit of 30 percent. The results of the comparison of the spiked and unspiked samples, and percent recovery calculations are shown in table 6. Each of the five spike compounds in the matrix spikes and matrix spike duplicates are labeled "spike" in Appendix B so that the values are not misinterpreted as environmental values.

**Table 6.** Matrix spikes and matrix-spike duplicates used to evaluate matrix effects and analytical reproducibility for surface-water samples analyzed for volatile organic compounds, Canal Creek area, Aberdeen Proving Ground, Maryland

[ $\mu$ g/L, micrograms per liter; %, percent; <, less than; control limits for percent recovery for 1,1-dichloroethene are 61–145 percent; for benzene are 76 to 127 percent; for trichloroethene are 71–120 percent; for toluene are 76 to 120 percent; and for chlorobenzene are 75 to 130 percent (Rose and Schroeder, 1995); control limit for relative percent difference between spike and duplicate is <30%]

	Sample date	Sample time	Matrix Spike Compounds (spike amount is 25.0 $\mu g/L$ )				
			1,1-Dichloro- ethene	Benzene	Trichloro- ethene	Toluene	Chloro- benzene
Set 1							
Environmental sample: SW050L	05/17/2000	1535	<0.5 µg/L	<0.5 μg/L	<0.5 μg/L	<0.5 µg/L	<0.5 µg/L
Matrix spike: SW050L-MS Percent recovery	05/17/2000	1535	27.4 μg/L 110%	25.4 μg/L 102%	24.8 μg/L 99.3%	27.7 μg/L 111%	26.1 μg/L 104%
Matrix spike duplicate: SW050L-MSD Percent recovery	05/17/2000	1535	32.0 μg/L 128%	28.3 μg/L 113%	28.0 μg/L 112%	30.5 μg/L 122%	28.1 μg/L 113%
Relative percent difference between spike and duplicate			15.4%	10.6%	12.0%	9.7%	7.6%
Set 2							
Environmental sample: SW060L	05/17/2000	1514	<0.5µg/L	<0.5µg/L	<0.5µg/L	<0.5µg/L	<0.5 µg/L
Matrix spike: SW060L-MS Percent recovery	05/17/2000	1514	23.6 μg/L 94.5%	26.3 μg/L 105%	25.3 μg/L 101%	26.9 μg/L 107%	25.6 μg/L 102%
Matrix spike duplicate: SW060L-MSD Percent recovery	05/17/2000	1514	30.2 μg/L 121%	26.1 μg/L 104%	26.4 μg/L 105%	28.5 μg/L 114%	25.6 μg/L 103%
Relative percent difference between spike and duplicate			24.4%	0.9%	4.3%	5.9%	0.0%

# Assessment of Volatile Organic Compounds in Surface Water

Eighty-four environmental VOC samples were collected, not including duplicate, triplicate, and quality-assurance samples. Of these 84 samples, 23 were collected in the nontidal part of the creek, and 61 were collected in the tidal part of Canal Creek. Overall, VOC concentrations in surfacewater samples ranged from below the reporting limit of 0.5 µg/L to a maximum of 50.2 µg/L for chloroform (CF) detected at site SW030 on November 5, 2000 (Appendix B). CF was the compound detected most frequently, and was detected in 55 percent (46 of 84 samples) of all the environmental samples. CT was detected in 56 percent of the surface-water samples in the tidal part of the creek (34 of 61 samples), but was detected in only 3 of 23 samples in the nontidal part of the creek. 1,1,2,2-Tetrachloroethane (TeCA) was detected in 43 percent of the tidal samples (26 of 61 samples), but was detected at only two nontidal sites, and only in November 1999. Three samples were collected in May 2000 from the Gunpowder River about 300 ft from the mouth of Canal Creek, and each sample showed VOC concentrations below detection levels. The distribution of total VOC concentrations in surface water between 1999 and 2000 during different seasons and tides at various locations is described, and the distribution and occurrence of individual VOCs are also described. An estimate of the contaminant load to the Gunpowder River is presented at the end of this section, along with the assumptions on which the calculations are based.

## **Distribution of Total Volatile Organic Compounds**

The distribution of total VOC concentrations is described in the following sections and shown in boxplots of the data. Boxplots are a type of graph that displays the distribution of the data based on the median, range, and 25th and 75th percentiles. Boxplots are useful for comparing the distributions of multiple data sets. Unrounded values were used to generate the boxplots (Appendix B values are rounded to the nearest 0.1  $\mu$ g/L), and analyses for duplicate samples were averaged together and presented as one sample so that distributions were not biased toward the duplicate results. Samples for which there were no detections of VOCs are interpreted in the boxplots as 0  $\mu$ g/L.

Comparison of Samples Collected in 1999 and 2000 During the summer (June-August) of 1999, the East Coast experienced a prolonged drought, with record and near-record short-term precipitation deficits on a local and regional scale resulting in drought emergencies being declared in several Mid-Atlantic States (National Oceanic and Atmospheric Administration, 1999). The study area was under drought conditions for much of 1999, but received a normal amount of precipitation during 2000.

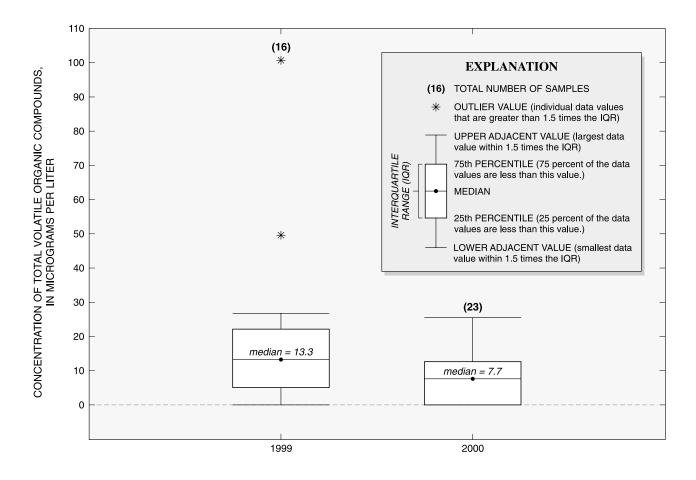
Olsen and Spencer (2000) published data from 16 surface-water samples collected at 5 sites (13 environmental and 3 duplicate samples) in March, May, July, and August of 1999. Four of the 5 sites (SW030, SW049.01, SW050,

and SW060) sampled during their investigation were also sampled during this investigation. Data from 12 of the 13 environmental samples collected from these 4 sites are included in the comparison of the distribution of total VOCs between 1999 and 2000 shown in figure 7. During this investigation, only one sampling round occurred during 1999, and three rounds occurred during 2000. The only data included in the comparison are from the 4 sites that were sampled during all sample rounds, in both this investigation and the previous study by Olsen and Spencer (2000).

The median of total VOC concentrations from the 4 sites was  $13.3 \,\mu\text{g/L}$  in  $16 \,\text{samples}$  collected in 1999, and was  $7.7 \,\mu\text{g/L}$  in  $23 \,\text{samples}$  collected in 2000. There were two outliers in the 1999 data whose concentrations were greater than  $1.5 \,\text{times}$  the interquartile range of all the 1999 data (fig. 7). This range indicates that there may be more variability of total VOC concentrations in a dry year (1999) than in a year with normal precipitation (2000), and may also indicate that during normal or wet years, greater dilution of the surface water may occur, reducing both the variability and overall concentrations of VOCs in the surface water. Although the two medians differed by  $5.6 \,\mu\text{g/L}$ , the ranked medians of the two distributions were not statistically different at a 95-percent confidence interval (Wilcoxonrank sum test, z = 1.7, p = 0.085).

**Comparison of Samples Collected During Different Seasons** Surface-water samples were collected in November 1999, and in February, May, and September 2000, roughly correlating to fall, winter, spring, and summer. The concentrations of total VOCs and CT, CF, and TeCA (the three most frequently detected compounds) for the four sampling rounds are shown in figures 8a, 8b, 8c, and 8d, respectively. Boxplots of the total VOC concentrations from the four sampling rounds are shown in figure 9 to show seasonal differences. The median concentration of total VOCs during the May 2000 sampling round was 1.6 µg/L, which is below the range of median concentrations (4.5 to 5.4 µg/L) for November, February, and September. In addition, the results from the November sampling showed higher variability because of the two samples that exceeded 20 µg/L of total VOCs. Although the highest number of samples was collected in May, the lowest median, range of concentrations, and variability were detected in comparison to the other three sampling rounds. The ranked medians of the four distributions, however, were not statistically different at a 95-percent confidence interval (Kruskal-Wallis rank sum test,  $\text{Chi}^2 = 2.87$ , degrees of freedom = 3, p = 0.41).

The distribution of total VOC concentrations by sampling date and tide stage for the five most commonly sampled sites is shown in figure 10. These data were compared to determine whether tide stage was a factor in the seasonal distribution of the data. Only data from these sites were used to prevent bias that could be introduced by data from sites not sampled as frequently. No noticeable difference was evident among total VOC concentrations collected at high, mid, or low tide. Samples collected in November showed the highest variability and had the highest VOC concen-



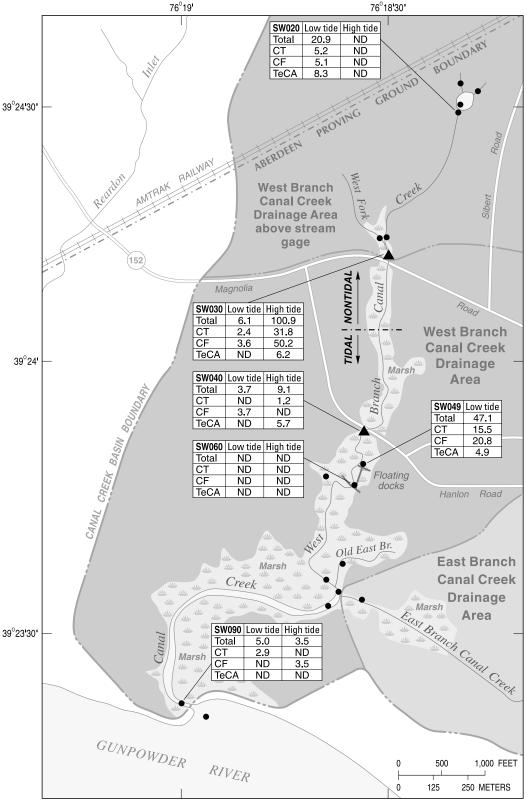
**Figure 7.** Difference between total volatile organic compound concentrations in surface water sampled in 1999 and 2000 at sites SW030, SW049.01, SW050, and SW060, Canal Creek, Aberdeen Proving Ground, Maryland (includes data from Olsen and Spencer, 2000).

trations, and the samples collected in May showed the lowest variability and the lowest VOC concentrations. These trends are consistent with those observed in the group of samples from all sites.

Comparison of Samples Collected During Different Tide Stages Surface-water samples were collected during high and low tides during all four sampling rounds. During the May and September rounds, samples also were collected during the outgoing mid-tide periods to assess the extent of contamination that may be leaving the creek and flowing into the Gunpowder River. The distribution of total VOCs during different tide stages for samples collected only in the tidal part of the creek during the four synoptic sampling rounds is shown in figure 11a. The distribution of total VOCs for samples collected during May and September is shown in figure 11b, so that the data are not biased by the sampling rounds when mid-tide samples were not collected.

A comparison of all samples that were collected only in the tidal part of the creek at different tide stages (fig. 11a) shows that the median concentrations of total VOCs were lowest at high tide (3.1  $\mu$ g/L), slightly higher at low tide (5.3  $\mu$ g/L), and slightly higher again at mid-tide (6.9  $\mu$ g/L). Outliers (values greater than 1.5 times the interquartile range) were present at high and low tides, but not at mid tide. Outliers are actual values because the samples were verified by the analyst and passed quality-assurance criteria, but the outliers should not be considered representative of the typical environmental conditions based on the majority of samples. The ranked medians of the three distributions in figure 11a were not statistically different at a 95-percent confidence interval (Kruskal-Wallis rank sum test,  $\text{Chi}^2 = 2.51$ , degrees of freedom = 2, p = 0.28).

A comparison of samples that were collected in May and September shows that concentrations at low and mid tides have similar distributions, but that concentrations at high tide are generally lower, with the exception of two outliers (fig. 11b). High-tide samples had a median VOC concentration of less than the detection limit. Dilution of the creek water by bay water at high tide is the most likely explanation for the generally lower concentrations found during high



## **EXPLANATION**

(All units are in micrograms per liter; ND, not detected)

**\$W090** SURFACE-WATER SAMPLING SITE NUMBER Total TOTAL VOLATILE ORGANIC COMPOUNDS

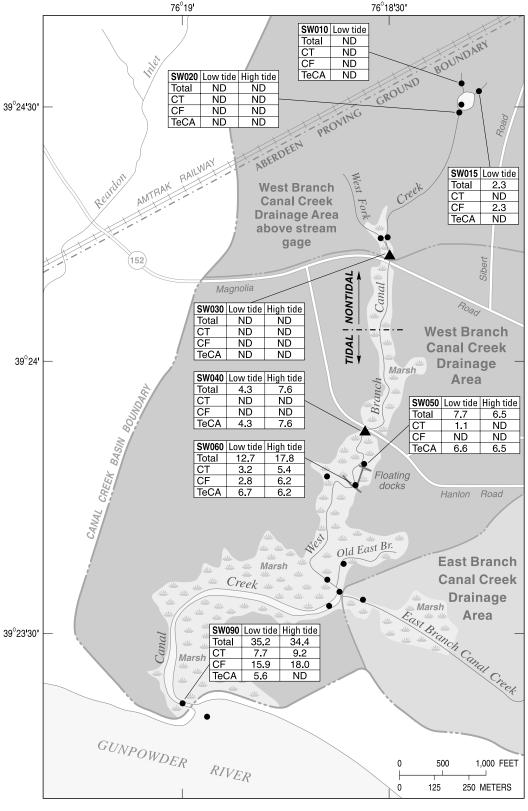
CT CARBON TETRACHLORIDE

CF CHLOROFORM

TeCA 1,1,2,2-TETRACHLOROETHANE

- ▲ STREAM OR TIDE GAGE AND SURFACE-WATER SAMPLING SITE
- SURFACE-WATER SAMPLING SITE

**Figure 8a.** Concentrations of total volatile organic compounds, carbon tetrachloride, chloroform, and 1,1,2,2-tetrachloroethane in surface water at Canal Creek, November 5, 1999, Aberdeen Proving Ground, Maryland.



## **EXPLANATION**

(All units are in micrograms per liter; ND, not detected)

**SW090** SURFACE-WATER SAMPLING SITE NUMBER TOTAL TOTAL VOLATILE ORGANIC COMPOUNDS

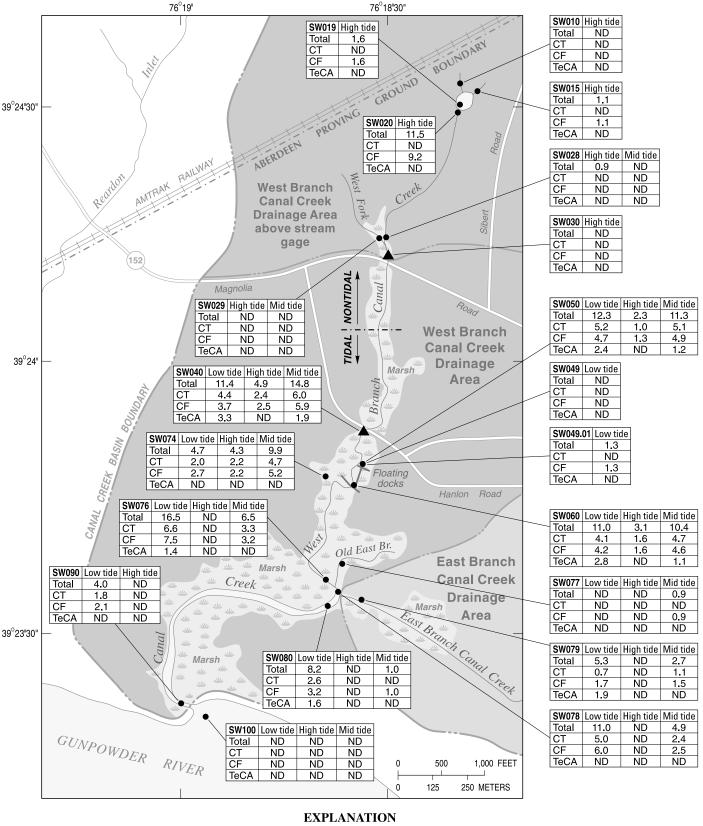
CT CARBON TETRACHLORIDE

CF CHLOROFORM
TeCA 1,1,2,2-TETRACHLOROETHANE

▲ STREAM OR TIDE GAGE AND SURFACE-WATER SAMPLING SITE

• SURFACE-WATER SAMPLING SITE

**Figure 8b.** Concentrations of total volatile organic compounds, carbon tetrachloride, chloroform, and 1,1,2,2-tetrachloroethane in surface water at Canal Creek, February 8, 2000, Aberdeen Proving Ground, Maryland.



(All units are in micrograms per liter; ND, not detected)

\$W090 SURFACE-WATER SAMPLING SITE NUMBER
Total TOTAL VOLATILE ORGANIC COMPOUNDS

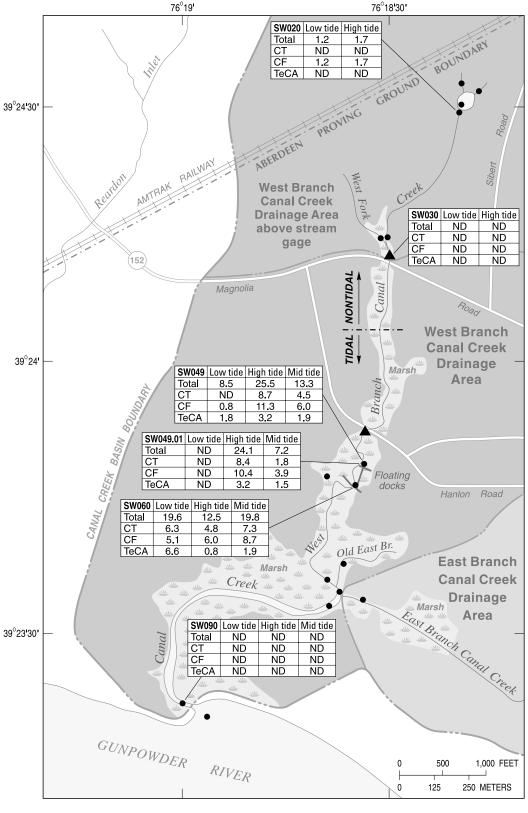
CT CARBON TETRACHLORIDE

CF CHLOROFORM

TeCA 1,1,2,2-TETRACHLOROETHANE

- ▲ STREAM OR TIDE GAGE AND SURFACE-WATER SAMPLING SITE
- SURFACE-WATER SAMPLING SITE

**Figure 8c.** Concentrations of total volatile organic compounds, carbon tetrachloride, chloroform, and 1,1,2,2-tetrachloroethane in surface water at Canal Creek, May 17, 2000, Aberdeen Proving Ground, Maryland.



## **EXPLANATION**

(All units are in micrograms per liter; ND, not detected)

**SW090** SURFACE-WATER SAMPLING SITE NUMBER TOTAL TOTAL VOLATILE ORGANIC COMPOUNDS

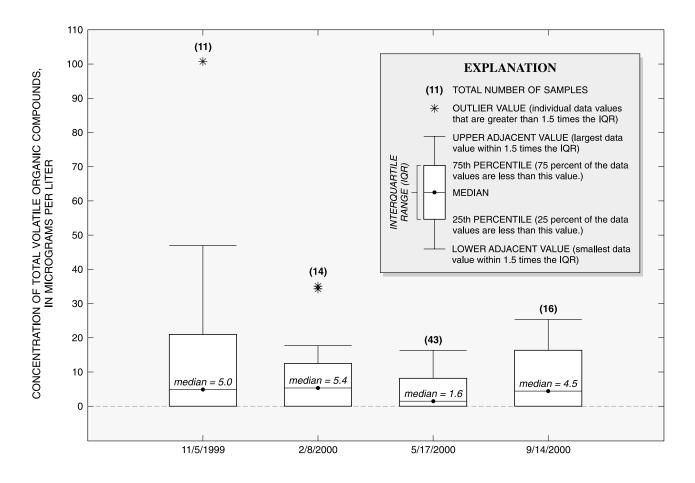
CT CARBON TETRACHLORIDE CF CHLOROFORM

TeCA 1,1,2,2-TETRACHLOROETHANE

▲ STREAM OR TIDE GAGE AND SURFACE-WATER SAMPLING SITE

SURFACE-WATER SAMPLING SITE

**Figure 8d.** Concentrations of total volatile organic compounds, carbon tetrachloride, chloroform, and 1,1,2,2-tetrachloroethane in surface water at Canal Creek, September 14, 2000, Aberdeen Proving Ground, Maryland.



**Figure 9.** Differences in total volatile organic compound concentrations between seasonal samples, Canal Creek, Aberdeen Proving Ground, Maryland.

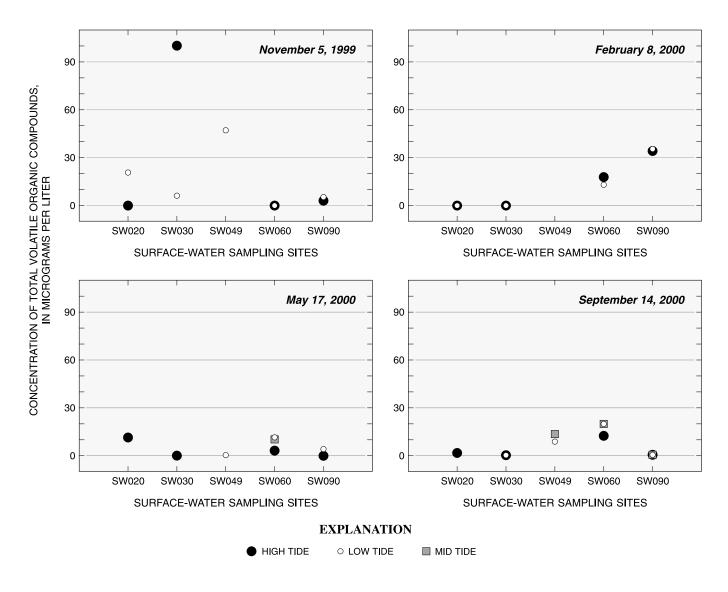
tide. At high tide, two samples had total VOC concentrations greater than 10 µg/L. The total VOC concentration at high tide was 12.5 µg/L in September at site SW060 at the floating bridge, and the concentration was 25.3 µg/L in September at site SW049.01 at a ground-water seep near the upstream set of docks. Each of these 2 sites are within an area of known ground-water contamination in the Canal Creek aquifer. The ranked medians of the three distributions shown in figure 11b, however, were not statistically different at a 95-percent confidence interval (Kruskal-Wallis rank sum test,  $\text{Chi}^2 = 2.95$ , degrees of freedom = 2, p = 0.23).

Comparison of Samples Collected at Different Locations The distribution of total VOCs varied with the distance along the length of the creek in the study area. Samples were collected from where the West Branch enters APG at site SW010, to a site located in the Gunpowder River at SW100 (fig. 3). There is known ground-water contamination in the Canal Creek aquifer in the vicinity of sites SW049, SW049.01, SW050, and SW060 (Olsen and others, 1997; Spencer and others, 2000) with total VOC concentrations in ground water as high as 50,700 µg/L at a depth of 12 ft near site SW060 (Phelan and others, 2001). Tidal fluctuations affect sites as far upstream as site SW040.

A comparison of the distributions of total VOCs by sampling site combining all data from the four synoptic sampling rounds is shown in figure 12. The concentrations of total VOCs, CT, CF, and TeCA at each site for each of the four sampling rounds are shown in figures 8a-d, respectively.

Beginning at the upstream end, inflows to the pond (sites SW010 and SW015; fig. 3) on West Branch had total VOC concentrations of less than 5  $\mu$ g/L. The outflow of the pond (site SW020) had higher concentrations than the inflow, and a wider range of variability, possibly because of the greater number of samples collected from that location. Seven samples were collected from site SW020; five had total VOC concentrations of less than 5  $\mu$ g/L, and two had total VOC concentrations of 11.5 and 20.9  $\mu$ g/L (fig. 12).

There are three sampling sites located immediately upstream of Magnolia Road—the West Branch at the stream gage (SW030), the west fork that feeds into the West Branch (SW029), and West Branch upstream of the west fork (SW028) (fig. 3; table 1). The West Branch at site SW030 was sampled more frequently than sites SW028 or SW029. Total VOC concentrations in two samples collected from sites SW028 and SW029 in May 2000 were less than 1  $\mu$ g/L for each sample. Seven samples were collected from the West Branch at site SW030. The first sample collected on



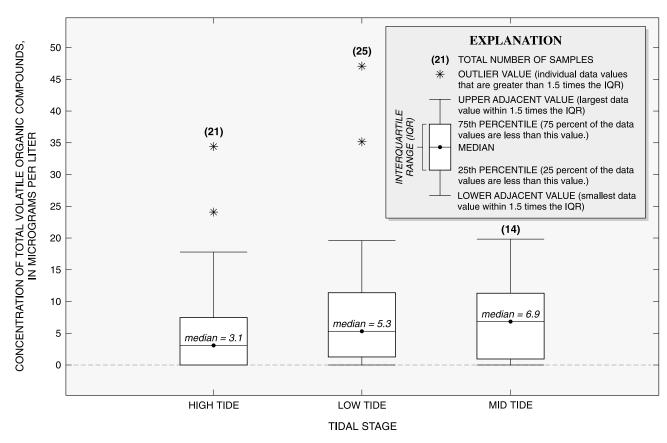
**Figure 10.** Distribution of total volatile organic compound concentrations by sampling date and tide stage for the five most commonly sampled sites, Canal Creek, Aberdeen Proving Ground, Maryland.

November 5, 1999, had total VOC concentrations of 6  $\mu$ g/L, and a sample collected 4 hours later had 101  $\mu$ g/L. The other five samples collected at site SW030 in February, May, and September 2000, however, had no detections. The data indicate that the VOC concentrations at site SW030 are highly variable, and the total VOC concentration of 101  $\mu$ g/L does not appear to reflect typical conditions.

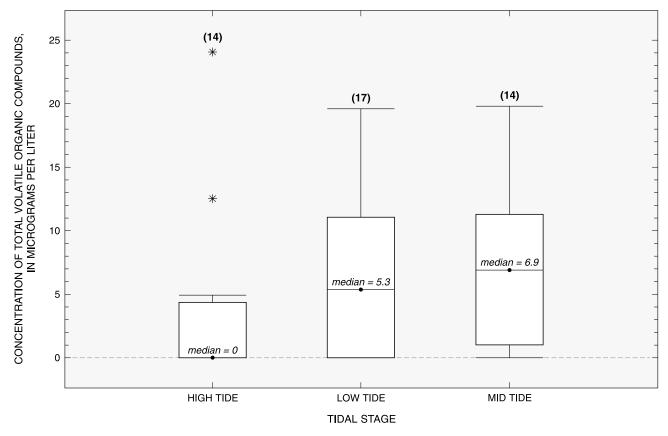
Site SW040 is located at the tide gage and is the farthest upstream tidal sampling site. Median total VOC concentrations at the site were 7.6  $\mu$ g/L, which was higher than sites upstream of SW040, but lower than three of the next four downstream sites (SW049, SW050, and SW060). The VOC concentrations at site SW040 could be higher than other upstream sites because of the tidal mixing and transport of contaminants from downstream, or because of a combination of tidal mixing and discharge of contaminated ground water in the vicinity of the tide gage. The next four downstream sites, SW049, SW049.01, SW050, and SW060 (fig. 3), are

located closest to the known areas of contamination of the Canal Creek aquifer, and generally have higher concentrations and a wider range of total VOCs in surface water than other sites sampled during this study (figs. 8a-d, and 12).

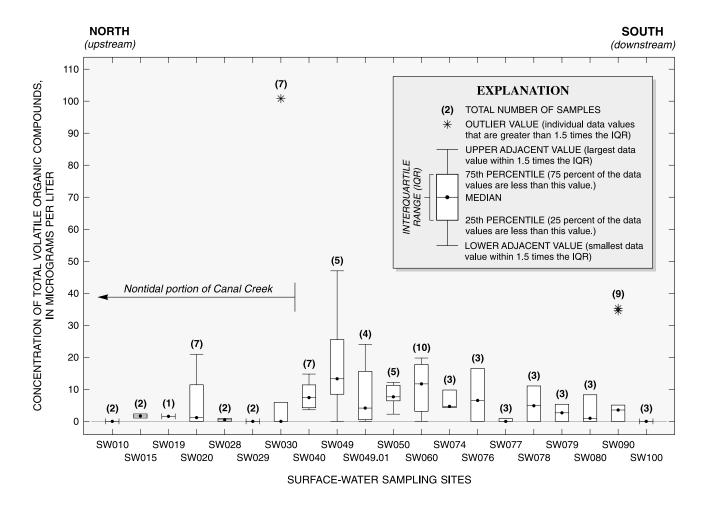
Site SW077 (fig. 3) is in the former channel of East Branch Canal Creek that was cut off from East Branch after stream channelization changed its location during the 1930s (Gary Nemeth, General Physics Corp., oral commun., 2001). Site SW079 is located about 200 ft up the new East Branch channel from the confluence with West Branch. Samples from sites SW077 (Old East Branch) and SW079 (new East Branch) had lower concentrations of total VOCs than sites in the West Branch located just upstream of each confluence during the May sampling, the only time these 2 sites were sampled (figs. 8c and 12). VOCs in the East Branch can originate either from tidal mixing with the West Branch, and /or known ground-water contamination plumes in the East Branch Canal Creek area (Lorah and Clark, 1996).



**Figure 11a.** Differences in total volatile organic compound concentrations between tide stages, November 1999 through September 2000, Canal Creek (*tidal portion only*), Aberdeen Proving Ground, Maryland.



**Figure 11b.** Differences in total volatile organic compound concentrations between tide stages, May and September 2000 only, Canal Creek (*tidal portion only*), Aberdeen Proving Ground, Maryland.



**Figure 12.** Distribution of total volatile organic compound concentrations at different sites, November 1999 through September 2000, Canal Creek, Aberdeen Proving Ground, Maryland.

Total VOC concentrations generally decrease with distance downstream from site SW060. The decrease in VOC concentrations is likely the result of a combination of less ground-water contamination discharging to the surface water in the area and more dilution from tidal flushing. Median total VOC concentrations were 3.5  $\mu$ g/L from nine samples collected at the mouth of Canal Creek where it discharges to the tidal Gunpowder River (fig. 12, site SW090). VOCs were below detection levels in the three surface-water samples collected in the Gunpowder River (site SW100) about 300 ft from the mouth of Canal Creek.

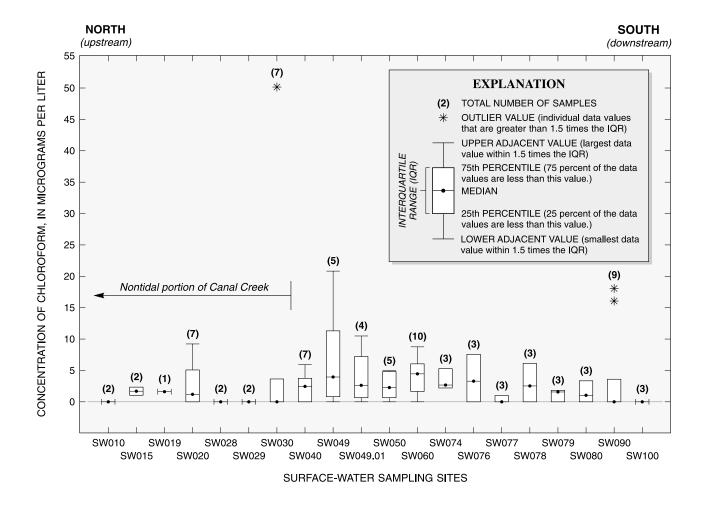
# **Distribution of Individual Volatile Organic Compounds**

The VOCs that were most frequently detected in the four synoptic sampling rounds and had the highest concentrations were chloroform (CF), carbon tetrachloride (CT), and 1,1,2,2-tetrachloroethane (TeCA). Trichloroethene (TCE) and tetrachloroethene (PCE) had the next highest frequency of detection, but none of the detections of TCE or PCE were greater than 10  $\mu$ g/L. CT was detected in only 3 of 23 samples from the nontidal part of the creek. TCE was detected in 2 of 23 samples at concentrations less than 5  $\mu$ g/L in the nontidal part of the creek. (Environmental

samples in which there were detections in both replicates were counted as one detection.)

In previous ground-water studies near sites SW050 and SW060, TeCA and TCE degraded through bioremediation processes to *cis-* and *trans-*1,2-dichloroethene (DCE), 1,2-dichloroethane (DCA), and vinyl chloride (VC) (Lorah and others, 1997). In this investigation, TeCA and TCE were detected frequently in the tidal part of the creek, but the daughter compounds *cis-* and *trans-*DCE and DCA were rarely detected, and another daughter compound, VC, was not detected at all.

**Chloroform** CF was detected in concentrations up to  $50.2 \,\mu\text{g/L}$  in the nontidal part of the creek, but with the exception of that one sample ( $50.2 \,\mu\text{g/L}$ ), concentrations in the nontidal part of the creek were less than  $10 \,\mu\text{g/L}$  (median was less than  $2 \,\mu\text{g/L}$ ). CF concentrations in the tidal parts of the creek were less than  $21 \,\mu\text{g/L}$ . Although a large number of CF detections were in the area of the floating docks, detections of CF also were observed as far upstream as the stormwater retention pond (site SW019) and as far downstream as the mouth of Canal Creek (site SW090), where it enters the Gunpowder River. CF was detected in 55 percent of all samples (46 out of 84 samples) and 62 percent of

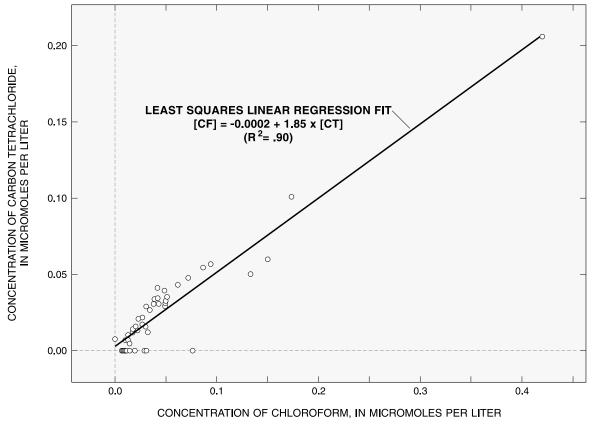


**Figure 13.** Distribution of chloroform concentrations at different sites, November 1999 through September 2000, Canal Creek, Aberdeen Proving Ground, Maryland.

the samples from the tidal part of the creek. The distribution and range of CF concentrations in surface water are shown in figure 13.

Of the samples in which CF was detected, 75 percent had detections of CT. The relation between concentrations of CF and CT is shown in figure 14. When CT was detected in surface-water samples, CF concentrations were typically twice as high as the CT concentrations (fig. 14). Phelan and others (2001) detected a CF concentration of 21,500 µg/L and a CT concentration of 10,300 µg/L near the top of the Canal Creek aguifer (12 ft below land surface at site HP01) about 100 ft south (downstream) of site SW060. The proportion of these two compounds in ground water at that site is very similar to the proportion in the surface-water samples. These compounds may have been disposed of together as solvents from the manufacturing of the chemicalfilled ordnance known to have been used in the area (Lorah and others, 1997). Although CT can chemically break down to form CF, concentrations of CF did not increase with a corresponding decline in CT concentrations, as would be expected during degradation processes.

**Carbon Tetrachloride** CT was the next most frequently detected VOC (after chloroform) in this study, and was found in 44 percent of all samples. It was detected in only 3 of 23 surface-water samples collected upstream of the tidal part of the creek (at sites SW020 and SW030), however. The distribution and range of CT concentrations in surface water are shown in figure 15. CT was detected in 56 percent of the surface-water samples (in 34 of 61 samples) in the tidal part of the creek. CT concentrations were generally highest in the vicinity of the floating docks, and concentrations decreased downstream from site SW060. The highest concentration of CT was 31.8 µg/L at site SW030 at Magnolia Road in November 1999, but CT was not detected at that site in subsequent sampling. The highest median concentration of CT was 4.4 µg/L at sites SW049 and SW060, located at the floating docks (fig. 3). CT concentrations as high as 10,300 µg/L were detected by Phelan and others (2001) near the top of the Canal Creek aguifer (at 12 ft below land surface), about 100 ft south of site SW060.



#### **EXPLANATION**

[CF] CONCENTRATION OF CHLOROFORM

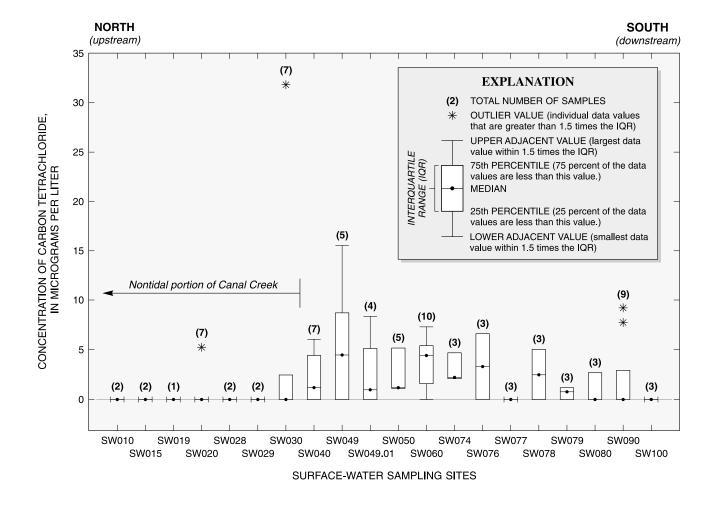
[CT] CONCENTRATION OF CARBON TETRACHLORIDE

**Figure 14.** Relation between concentrations of chloroform and carbon tetrachloride in surface water, Canal Creek, Aberdeen Proving Ground, Maryland.

1,1,2,2-Tetrachloroethane TeCA was detected in 43 per-cent of the tidal samples (in 26 of 61 samples), but was detected in only 2 of 23 nontidal samples (9 percent). The distribution and range of concentrations of TeCA in surface water are shown in figure 16. Concentrations of TeCA were generally less than concentrations of CF or CT, and the highest median concentration for any individual site was 3.2 µg/L at the tide gage at site SW040. TeCA was detected at sites SW079 (East Branch) and SW080 (just downstream of East Branch) at concentrations of 2 µg/L or less (fig. 16), indicating a possible source in the East Branch Canal Creek Basin or in the ground water near site SW079. Median concentrations of TeCA were below detection levels in the surface-water samples in West Branch downstream of site SW060 (floating bridge), indicating that volatilization and /or dilution resulted before the contaminant reached the confluence with the East Branch or the Gunpowder River.

# **Estimated Volatile Organic Compound Load to the Gunpowder River**

An estimate of the contaminant load to the Gunpowder River is presented in this section, along with the assumptions on which the calculations are based. Contaminant load is estimated in this report on the basis of typical VOC concentrations in Canal Creek, and estimated average creek discharge at the mouth. Typically, loads would be calculated based on concentrations and discharge rates from the mouth of the creek. Because relatively clean tidal inflow from the Gunpowder River dilutes the creek water near the mouth, and samples taken from the mouth can be more representative of water that had just entered the creek than water that had flowed through the basin, the median concentrations for all tidal sites were used to represent typical concentrations discharging from the creek. Total discharge of surface water from Canal Creek to the Gunpowder River on any given day, however, is extremely variable primarily because of the effects of typical tidal fluctuations, and changes in regional rainfall, wind direction, and wind speed.



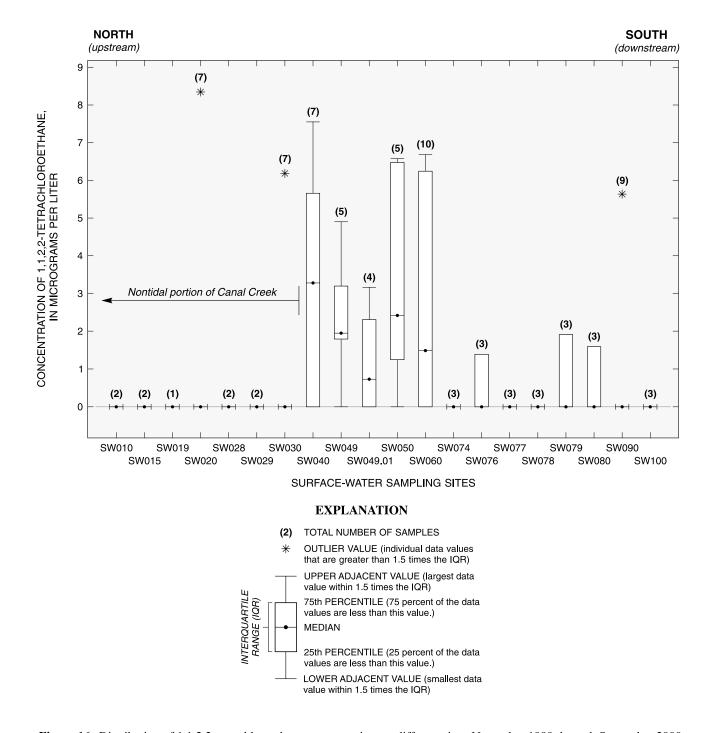
**Figure 15.** Distribution of carbon tetrachloride concentrations at different sites, November 1999 through September 2000, Canal Creek, Aberdeen Proving Ground, Maryland.

### **Estimated Volatile Organic Compound**

Concentrations For the following calculations, overall concentrations of VOCs in the tidal inflow from the Gunpowder River to Canal Creek are assumed to be essentially zero (three samples taken at site SW100 had no detections). The con-centrations of individual VOCs in the tidal part of Canal Creek are assumed to be the medians of all values for all constituents found in 85 surface-water samples collected

only from the tidal part of the creek (sites SW040 through SW090) from February 1999 through September 2000. These 85 samples include those collected during this investigation, those presented in Olsen and Spencer (2000), and miscellaneous sites included in Appendix B of this report. The median concentrations for each compound are as follows:

COMPOUND	CONCENTRATION [in micrograms per liter, or µg/L]
CF	2.66
CT	2.34
TeCA	1.24
Other VOCs (primarily PCE and TCE)	0.28
Total VOCs	6.52 μg/L



**Figure 16.** Distribution of 1,1,2,2-tetrachloroethane concentrations at different sites, November 1999 through September 2000, Canal Creek, Aberdeen Proving Ground, Maryland.

**Estimated Discharge Volume** The following assumptions are used to estimate the amount of water discharging from Canal Creek for a typical tide cycle:

- (1) The area of Canal Creek tidal wetlands that drain into the Gunpowder River is approximately 0.17 mi<sup>2</sup> (445,000 m<sup>2</sup>, or square meters).
- (2) The range of water levels in the creek channel during a typical tidal cycle is from 0.5 to 1.5 ft, resulting in a typical difference in depth at the creek channel of 1 ft (approximately 0.3 m, or meters).
- (3) Water-level changes through a tide cycle are about 0 ft at the edges of the wetland and about 1 ft at the channel, resulting in an average change in water depth over the entire 0.15-mi<sup>2</sup> (445,000 m<sup>2</sup>) area of about 0.5 ft (0.15 m).
- (4) On the basis of the dimensions specified in 1–3, the volume of water that exits Canal Creek during each tidal cycle is estimated to be 66,750,000 liters based on the following:

 $(Area) \times (Change in depth) = (Volume)$ 

 $(445,000 \text{ m}^2) \times 0.15 \text{ m} = 66,750 \text{ m}^3 \text{ (cubic meters)}$ 

Multiplying 66,750 m<sup>3</sup> × 
$$\frac{1,000 \text{ L}}{1\text{m}^3}$$
 = 66,750,000 liters

- (5) One tidal cycle takes place every 0.52 day.
- (6) The mean daily discharge from the West Branch Canal Creek measured at the Magnolia Road gaging station is 1.19 ft<sup>3</sup>/s (table 1), which represents less than 0.1 percent of the amount of water actually discharging to the Gunpowder River because of tidal flushing each day. Therefore, of this total amount, the amount of fresh surface water discharging to the tidal part of the creek was not a factor in the calculation of VOC loads to the Gunpowder River.

**Load Calculation** Contaminant loads are generally calculated by multiplying contaminant concentrations by the volume discharged. Based on the previous assumptions, VOC loads may be calculated as follows:

Compound	Concentration, median (micrograms per liter)	Volume discharged per tide (liters)	Load per tide <sup>1</sup> (micrograms)	Load per tide <sup>2</sup> (grams)	Load per day <sup>3</sup> (grams)	Load per day <sup>4</sup> (kilograms)	Load per day <sup>5</sup> (pounds)	Load per year <sup>6</sup> (pounds)
CF <sup>7</sup>	2.66	66,750,000	177,555,000	177.6	341.5	0.34	0.75	275
CT <sup>8</sup>	2.34	66,750,000	156,195,000	156.2	300.4	.30	.66	242
TeCA 9	1.24	66,750,000	82,770,000	82.8	159.2	.16	.35	128
Other VOCs <sup>10</sup>	0.28	66,750,000	18,690,000	18.7	35.9	.04	.08	29
<b>Total VOCs</b>	6.52		435,210,000	435.2	836.9	0.84	1.85	674

<sup>&</sup>lt;sup>1</sup> Load per tide = Concentration x liters discharged.

33

<sup>&</sup>lt;sup>2</sup> Load per tide = Micrograms per tide / 1,000,000 micrograms per gram.

 $<sup>^{3}</sup>$  Load per day = Grams per tide / 0.52 tide cycles per day.

<sup>&</sup>lt;sup>4</sup> Load per day = Grams per day / 1,000 grams per kilogram.

<sup>&</sup>lt;sup>5</sup> Load per day = Kilograms per day x 2.205 pounds per kilogram.

<sup>&</sup>lt;sup>6</sup> Load per year = Pounds per day x 365 days per year.

<sup>&</sup>lt;sup>7</sup> Chloroform.

<sup>&</sup>lt;sup>8</sup> Carbon tetrachloride.

<sup>&</sup>lt;sup>9</sup> 1,1,2,2-tetrachloroethane.

<sup>&</sup>lt;sup>10</sup> Volatile organic compounds, primarily tetrachloroethene and trichloroethene.

The estimated long-term load of total VOCs to the Gunpowder River can average approximately 1.85 pounds per day, or 674 pounds per year. This calculation is a good approximation of the amount of contamination that may be reaching the Gunpowder River, but should be used with caution because of the assumptions on which it was based.

# **Summary and Conclusions**

Since 1917, Aberdeen Proving Ground, Maryland, has been primarily a weapons, ordnance, and chemical-warfare research and development center for the U.S. Army. Most of Aberdeen Proving Ground's chemical-manufacturing and munitions-filling plants were located in the area between the West Branch and East Branch of Canal Creek. Waste from many of these activities was discharged into the East and West Branch Canal Creek either directly through overland runoff, sewer discharges, or burial, or indirectly through the discharge of contaminated ground water into the wetland areas. This investigation was performed in cooperation with the U.S. Army Garrison, Aberdeen Proving Ground, Environmental Conservation and Restoration Division, and supports the original investigation by the U.S. Geological Survey that began in 1992 to determine the distribution, fate, and transport of chlorinated volatile organic compounds in ground water.

Surface-water samples were collected for volatile organic compounds collected in the Canal Creek area of Aberdeen Proving Ground, Maryland, from November 1999 through September 2000, to assess the occurrence and distribution of volatile organic compounds. This report describes the effects of below-normal and normal precipitation, seasons, tide stages, and location on concentrations of volatile organic compounds in surface water, and provides estimates of loads to the tidal Gunpowder River.

Surface-water samples were collected for volatile organic compounds at 6 sites in November 1999 and September 2000, at 8 sites in February 2000, and at 20 sites in the May 2000 sampling round. Eighty-four water samples were analyzed, not counting duplicate, triplicate, or quality-assurance samples. The samples included 32 duplicate pairs and one triplicate set, and 11 blank samples. Samples were analyzed for volatile organic compound concentrations using a purge-and-trap capillary gas chromatograph with a mass-selective detector. Thirteen different volatile organic compounds were detected in concentrations above the detection limit.

Comparisons between 1999 and 2000 indicate that during the drier year (1999), volatile organic compound concentrations were slightly higher and had greater variability than during 2000. A comparison of all samples that were collected only in the tidal part of the creek at different tide stages shows that the median concentrations of total volatile organic compounds were lowest at high tide

(3.1 micrograms per liter), slightly higher at low tide (5.3 micrograms per liter), and highest at mid-tide (6.9 micrograms per liter). Volatile organic compound concentrations were lower and had somewhat lower variability during May than during other months when samples were collected. Volatile organic compound concentrations in surface water were highest in the reaches of the creek adjacent to the areas with the highest known levels of ground-water contamination, primarily in the West Branch Canal Creek between sampling sites SW040 and SW076. Volatile organic compounds were detected at all surfacewater sites in the East and West Branch Canal Creek with the exception of the most upstream site (SW010) and the Gunpowder River site (SW100).

Concentrations of volatile organic compounds in surfacewater samples ranged from below the reporting limit of 0.5 micrograms per liter to a maximum of 50.2 micrograms per liter for chloroform, detected at site SW030 on November 5, 2000. Chloroform was the compound detected most frequently, and was detected in 55 percent of the environmental samples. Carbon tetrachloride was detected in 56 percent of the surface-water samples from the tidal part of Canal Creek, but was only detected in 3 of 23 samples from the nontidal part of the creek. 1,1,2,2-Tetrachloroethane was detected in 43 percent of the tidal samples (26 out of 61), but was detected in only 2 of 26 samples from the nontidal sites. These compounds were also the major contaminants found in the Canal Creek aquifer during previous studies in the area. Each of three samples collected in May 2000 from the Gunpowder River about 300 feet from the mouth of Canal Creek had volatile organic compound concentrations below detection levels. Estimated long-term load of total volatile organic compounds discharging to the Gunpowder River can average approximately 1.85 pounds per day, or 674 pounds per year. Although natural-attenuation processes in the study area such as biodegradation are highly effective at reducing contaminant concentration in ground water before it discharges to the creek, natural attenuation is not 100 percent effective at all locations or under all tidal, seasonal, and climatic conditions as indicated by the detection of volatile organic compounds in Canal Creek.

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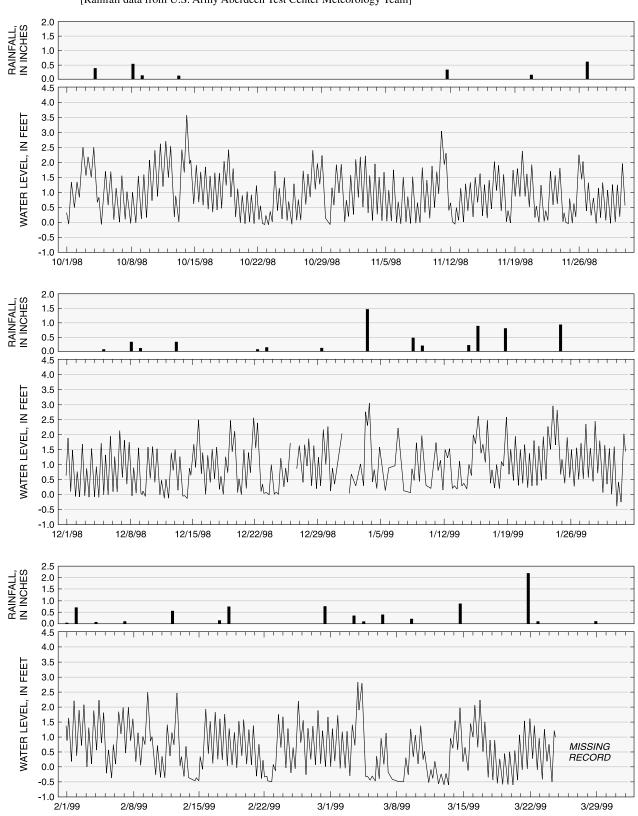
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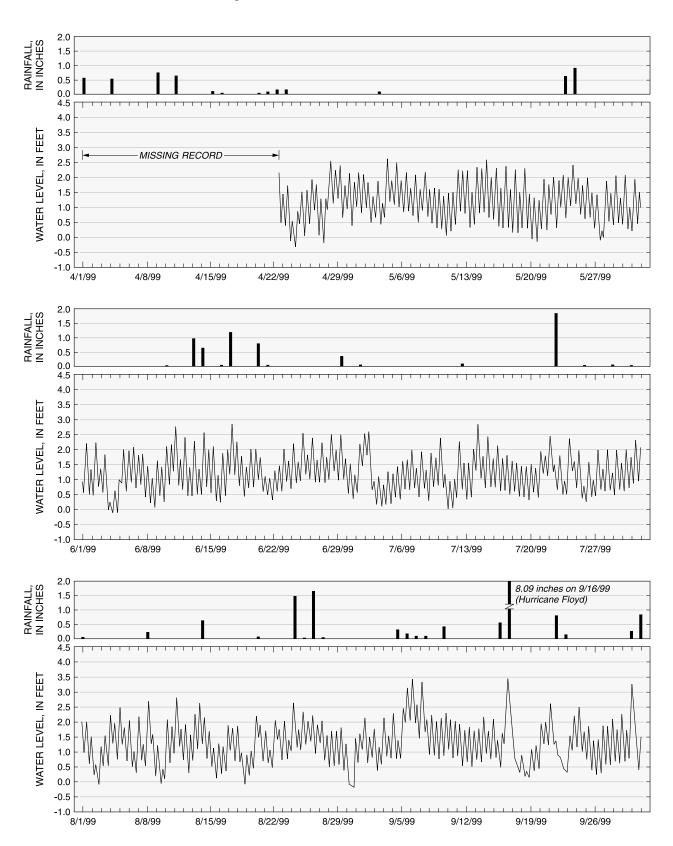
Appendixes A and B Follow

**Appendix A.** Daily rainfall totals at Aberdeen Proving Ground, and tidal fluctuations at the Hanlon Road tide gage, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, October 1, 1998 to September 30, 2000

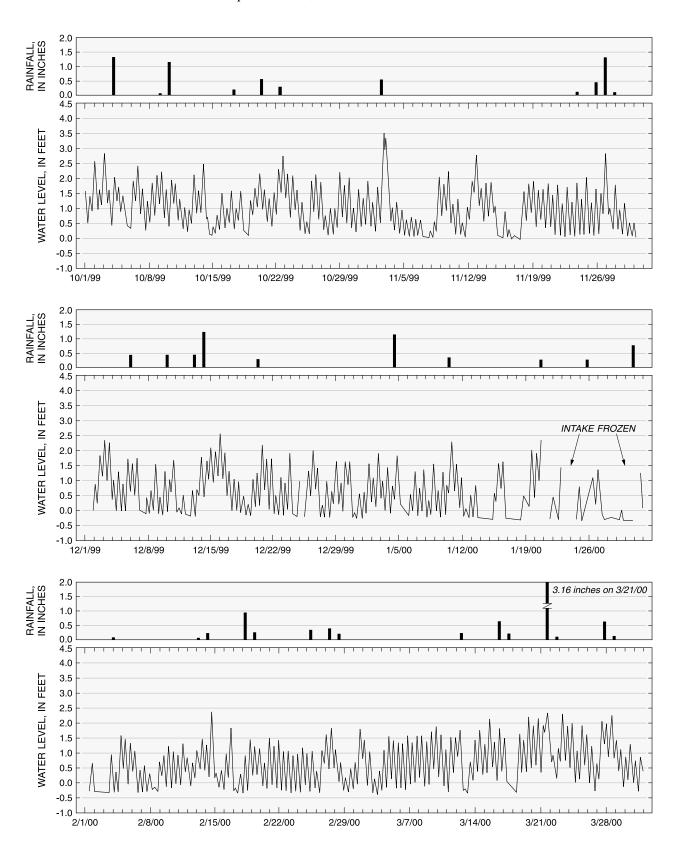
[Rainfall data from U.S. Army Aberdeen Test Center Meteorology Team]



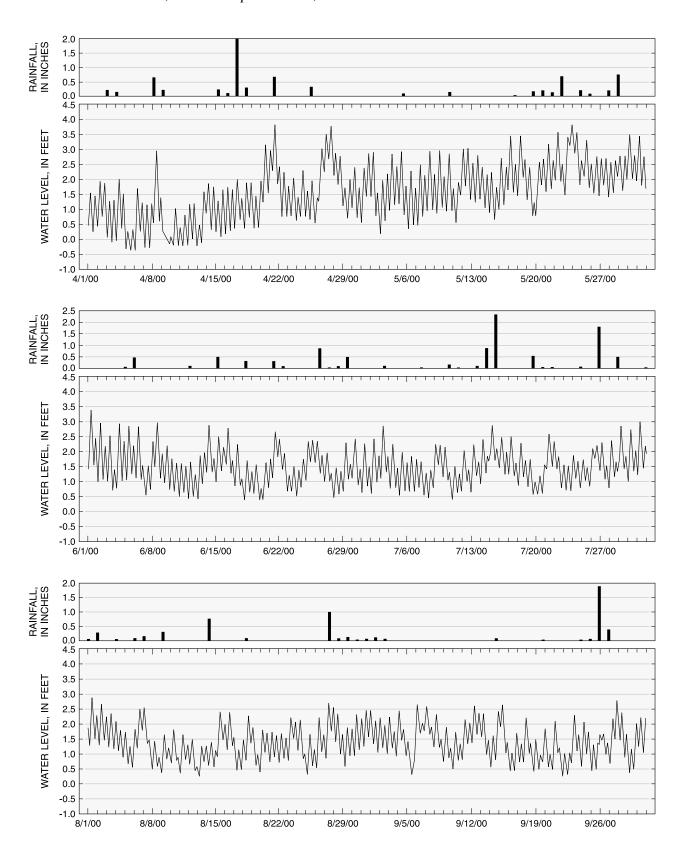
**Appendix A.** Daily rainfall totals at Aberdeen Proving Ground, and tidal fluctuations at the Hanlon Road tide gage, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, October 1, 1998 to September 30, 2000 -- Continued



**Appendix A.** Daily rainfall totals at Aberdeen Proving Ground, and tidal fluctuations at the Hanlon Road tide gage, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, October 1, 1998 to September 30, 2000 -- Continued



**Appendix A.** Daily rainfall totals at Aberdeen Proving Ground, and tidal fluctuations at the Hanlon Road tide gage, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, October 1, 1998 to September 30, 2000 -- Continued



**Appendix B.** Organic constituents in surface-water samples from the Canal Creek area, Aberdeen Proving Ground, Maryland, November 1999 through September 2000

[Sample names are a combination of the site name from which the sample was collected, followed by the letters H, M, or L. The letters indicate whether the sample was collected at high tide (H), mid tide (M), or low tide (L);  $\mu$ S/cm, microsiemens per centimeter;  $^{\circ}$ C, degrees Celsius;  $\mu$ g/L, micrograms per liter; na, not applicable; <, less than; –, no data; **E**, estimated value; spike, compound spiked and analyzed for quality assurance (see table 6); \*, water trapped under docks; MS, matrix spike; MS-D, matrix spike duplicate]

				FIE	LD PARAMI	ETERS	CHLORINATED ETHANES			
Sample name	Tide	Date collected	Time collected	Replicate number	Specific conduct- ance (µS/cm)	pH (standard units)	Tem- perature (°C)	1,1,2,2- Tetra- chloro- ethane (µg/L)	1,1,2- Trichloro- ethane (µg/L)	1,2- Dichloro- ethane (µg/L)
				November 1	000 Commline	Event				
SW020L	Low	11/05/1999	1254	November 1	999 Sampling	Event		8.3	<1.0	<1.0
SW020L SW020L	Low	11/05/1999	1254	2	_	_	_	8.4	<1.0	<1.0
SW020L SW020H	High	11/05/1999	1630	1	_	_	_	<1.0	<1.0	<1.0
SW020H	High	11/05/1999	1630	1	_	_	_	<1.0	<1.0	<1.0
5 W 02011	High	11/03/1999	1030	1	_	_	_	<1.0	<1.0	<1.0
SW030L	Low	11/05/1999	1245	na	_	_	_	<1.0	<1.0	<1.0
SW030H	High	11/05/1999	1640	na	-	-	-	6.2	<1.0	<1.0
SW040L	Low	11/05/1999	1315	1	_	_	_	<1.0	<1.0	<1.0
SW040L	Low	11/05/1999	1315	2	_	_	_	<1.0	<1.0	<1.0
SW040H	High	11/05/1999	1650	1	_	_	_	8.0	<1.0	<1.0
SW040H	High	11/05/1999	1650	2	_	_	_	3.4	2.3	<1.0
SW049L	Low	11/05/1999	1246	na	-	_	_	4.9	<1.0	<1.0
SW060L	Low	11/05/1999	1305	na	_	_	_	<1.0	<1.0	<1.0
SW060H	High	11/05/1999	1700	na	_	_	_	<1.0	<1.0	<1.0
5 11 00011	111511	11/03/17/7	1700	II.				11.0	11.0	11.0
SW090L	Low	11/05/1999	1300	na	_	_	_	<1.0	<1.0	<1.0
SW090H	High	11/05/1999	1710	1	_	_	_	<1.0	<1.0	<1.0
SW090H	High	11/05/1999	1710	2	-	-	-	<1.0	<1.0	<1.0
				February 20	000 Sampling	Event				
SW010L	Low	02/08/2000	1615	1	231		5.1	<1.0	<1.0	<1.0
SW010L	Low	02/08/2000	1615	2	-	_	-	<1.0	<1.0	<1.0
SW015L	Low	02/08/2000	1625	na	-	_	3.4	<1.0	<1.0	<1.0
SW020H	High	02/08/2000	1050	na	773	_	1.3	<1.0	<1.0	<1.0
SW020L	Low	02/08/2000	1405	1	666	_	2.9	<1.0	<1.0	<1.0
SW020L	Low	02/08/2000	1405	2	_	_	_	<1.0	<1.0	<1.0
SW028L	Low	02/08/2000	1555	na	624	_	3.0	_	_	_
SW029L	Low	02/08/2000	1550	na	151	_	2.9	_	_	_
SW030H	High	02/08/2000	1035	na	540	_	1.0	<1.0	<1.0	<1.0
SW030L	Low	02/08/2000	1545	1	474	_	5.4	<1.0	<1.0	<1.0
SW030L	Low	02/08/2000	1545	2	_	_	-	<1.0	<1.0	<1.0
SW040H	High	02/08/2000	1020	1	785	-	2.7	7.5	<1.0	<1.0
SW040H	High	02/08/2000	1020	2	_	-	-	7.6	<1.0	<1.0
SW040L	Low	02/08/2000	1530	na	756	_	-	4.3	<1.0	<1.0
SW050H	High	02/08/2000	1000	1	793	_	2.0	6.2	<1.0	<1.0
SW050H	High	02/08/2000	1000	2	_	_	_	6.8	<1.0	<1.0
SW050L	Low	02/08/2000	1440	1	540	_	6.9	5.7	<1.0	<1.0
SW050L	Low	02/08/2000	1440	2	_	_	_	7.4	<1.0	<1.0

	CHL	ORINATED	ETHENES			PRINATED THANES		TIONAL VOL		
Tetra- chloro- ethene (µg/L)	Tri- chloro- ethene (µg/L)	cis-1,2- Di- chloro- ethene (μg/L)	trans- 1,2-Di- chloro- ethene (µg/L)	Vinyl chloride (µg/L)	Carbon tetra- chloride (µg/L)	Chloro- form (µg/L)	Dichloro- difluoro- methane (µg/L)	Bromo- dichloro- methane (µg/L)	Toluene (μg/L)	Sample name
<1.0	2.2	<1.0	<1.0	<1.0	4.8	5.1	< 5.0	<1.0	<1.0	SW020L
<1.0	2.4	<1.0	<1.0	<1.0	5.7	5.0	< 5.0	<1.0	<1.0	SW020L
<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	< 5.0	<1.0	<1.0	SW020H
<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<5.0	<1.0	<1.0	SW020H
<1.0	<1.0	<1.0	<1.0	<1.0	2.4	3.6	< 5.0	<1.0	<1.0	SW030L
8.7	4.0	<1.0	<1.0	<1.0	31.8	50.2	<5.0	<1.0	<1.0	SW030H
0.7		12.0	12.0	11.0	21.0	20.2		11.0	11.0	5 11 05 011
<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	3.2	< 5.0	<1.0	<1.0	SW040L
<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	4.2	< 5.0	<1.0	<1.0	SW040L
<1.0	2.3	<1.0	<1.0	<1.0	2.3	<1.0	< 5.0	<1.0	<1.0	SW040H
<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	< 5.0	<1.0	<1.0	SW040H
3.6	2.3	<1.0	<1.0	<1.0	15.5	20.8	<5.0	<1.0	<1.0	SW049L
<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<5.0	<1.0	<1.0	SW060L
<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<5.0	<1.0	<1.0	SW060H
<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	₹3.0	<1.0	<1.0	5 ** 00011
<1.0	2.1	<1.0	<1.0	<1.0	2.9	<1.0	< 5.0	<1.0	<1.0	SW090L
<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	3.2	< 5.0	<1.0	<1.0	SW090H
<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	3.7	<5.0	<1.0	<1.0	SW090H
<1.0	<1.0	<1.0	<2.0	<1.0	<1.0	<1.0	<5.0	<1.0	<1.0	SW010L
<1.0	<1.0	<1.0	< 2.0	<1.0	<1.0	<1.0	< 5.0	<1.0	<1.0	SW010L
<1.0	<1.0	<1.0	<2.0	<1.0	<1.0	2.3	<5.0	<1.0	<1.0	SW015L
1.0	1.0	1.0	2.0	1.0	1.0	1.0	5.0	1.0	1.0	GHAOGOTA
<1.0	<1.0	<1.0	<2.0	<1.0	<1.0	<1.0	<5.0	<1.0	<1.0	SW020H
<1.0	<1.0	<1.0	<2.0	<1.0	<1.0	<1.0	<5.0	<1.0	<1.0	SW020L
<1.0	<1.0	<1.0	<2.0	<1.0	<1.0	<1.0	<5.0	<1.0	<1.0	SW020L
-	_	-	-	-	-	-	-	-	_	SW028L
-	-	_	-	-	-	-	-	-	-	SW029L
<1.0	<1.0	<1.0	<2.0	<1.0	<1.0	<1.0	< 5.0	<1.0	<1.0	SW030H
<1.0	<1.0	<1.0	<2.0	<1.0	<1.0	<1.0	< 5.0	<1.0	<1.0	SW030L
<1.0	<1.0	<1.0	<2.0	<1.0	<1.0	<1.0	< 5.0	<1.0	<1.0	SW030L
,1 O	.1.0	.1.0	-0.0	-1.0	.1.0	<sub>2</sub> 1.0	.E.O	.1.0	-1.0	CWOACIT
<1.0	<1.0	<1.0	<2.0	<1.0	<1.0	<1.0	<5.0	<1.0	<1.0	SW040H
<1.0	<1.0	<1.0	<2.0	<1.0	<1.0	<1.0	<5.0	<1.0	<1.0	SW040H
<1.0	<1.0	<1.0	<2.0	<1.0	<1.0	<1.0	<5.0	<1.0	<1.0	SW040L
<1.0	<1.0	<1.0	< 2.0	<1.0	<1.0	<1.0	< 5.0	<1.0	<1.0	SW050H
<1.0	<1.0	<1.0	< 2.0	<1.0	<1.0	<1.0	< 5.0	<1.0	<1.0	SW050H
<1.0	<1.0	<1.0	< 2.0	<1.0	2.3	<1.0	< 5.0	<1.0	<1.0	SW050L
<1.0	<1.0	<1.0	< 2.0	<1.0	<1.0	<1.0	< 5.0	<1.0	<1.0	SW050L

**Appendix B.** Organic constituents in surface-water samples from the Canal Creek area, Aberdeen Proving Ground, Maryland, November 1999 through September 2000—Continued

				Replicate number	FIE	LD PARAMI	ETERS	CHLC	ORINATED E	THANES
Sample name	Tide	Date collected	Time collected		Specific conduct- ance (µS/cm)	pH (standard units)	Tem- perature (°C)	1,1,2,2- Tetra- chloro- ethane (µg/L)	1,1,2- Trichloro- ethane (µg/L)	1,2- Dichloro- ethane (µg/L)
				February 20	000 Sampling	Event—Cont	inued			
SW060H	High	02/08/2000	945	na		_	1.4	6.2	<1.0	<1.0
SW060L	Low	02/08/2000	1425	1	788	_	7.3	6.3	<1.0	<1.0
SW060L	Low	02/08/2000	1425	2	-	_	-	7.1	<1.0	<1.0
SW090H	High	02/08/2000	920	na	1,620	_	0.5 .9	<1.0 5.6	<1.0	<1.0 <1.0
SW090L	Low	02/08/2000	1345	na	1,400	_	.9	3.0	<1.0	<1.0
				Quality-Ass	urance Sampl	les, February	2000			
Travel Blank	_	02/08/2000	850	_	_	_	_	<1.0	<1.0	<1.0
Trip Blank	-	02/08/2000	851	-	_	-	-	<1.0	<1.0	<1.0
				May 2000 Sa	ampling Even	ıt				
SW010H	High	05/17/2000	1010	na	_	_	-	<1.0	<1.0	< .5
SW015H	High	05/17/2000	957	na	-	_	-	<1.0	<1.0	< .5
SW019H	High	05/17/2000	945	na	-	_	-	<1.0	<1.0	< .5
SW020H	High	05/17/2000	930	na	_	_	_	<1.0	<1.0	< .5
SW028H	High	05/17/2000	859	na	_	_	_	<1.0	<1.0	.9
SW028M	Mid	05/17/2000	1155	na	_	_	_	<1.0	<1.0	< .5
SW029H	High	05/17/2000	908	na	_	-	-	<1.0	<1.0	< .5
SW029M	Mid	05/17/2000	1200	na	_	-	_	<1.0	<1.0	< .5
SW030H	High	05/17/2000	846	1	_	_	_	<1.0	<1.0	< .5
SW030H	High	05/17/2000	846	2	_	_	_	<1.0	<1.0	< .5
CM/04011	TT: . 1.	05/17/2000	927					.1.0	.1.0	
SW040H	High	05/17/2000	826	na	_	_	_	<1.0	<1.0	< .5
SW040M	Mid	05/17/2000	1145	na	_	_	_	1.9	1.1	< .5
SW040L	Low	05/17/2000	1550	na	_	_	_	3.3	<1.0	< .5
SW049L	Low	05/17/2000	1545	1	_	_	_	<1.0	<1.0	< .5
SW049L	Low	05/17/2000	1545	2	_	-	-	<1.0	<1.0	< .5
SW049.01L	Low	05/17/2000	1552	na	598	6.6	24.4	<1.0	<1.0	< .5
SW050H	High	05/17/2000	827	1	_	_	_	<1.0	<1.0	< .5
SW050H	High	05/17/2000	827	2	695	_	20.6	<1.0	<1.0	< .5
SW050M	Mid	05/17/2000	1135	na	651	- 7.1	20.9	1.2	<1.0	< .5
SW050M SW050L	Low	05/17/2000	1535		502	7.1	24.7	2.4	<1.0	< .5
SW050L SW050L-MS	Low	05/17/2000	1535	na				2.4	<1.0	< .5
SW050L-MS-D		05/17/2000	1535	na na	_	_	_	2.5	<1.0	< .5 < .5
SW060H	High	05/17/2000	825	1	702	_	_	<1.0	<1.0	< .5
SW060H	High	05/17/2000	825	2	-	_	-	<1.0	<1.0	< .5
SW060M	Mid	05/17/2000	1140	na	641	- 5.0	21.3	1.1	<1.0	< .5
SW060L	Low	05/17/2000	1514	na	509	7.3	25.0	2.8	<1.0	< .5
SW060L-MS	Low	05/17/2000	1514	1	_	_	_	2.0	<1.0	< .5
SW060L-MS	Low	05/17/2000	1514	2	_	_	_	2.4	<1.0	< .5

Sample name		IONAL VOL		RINATED HANES			ETHENES	PRINATED I	CHLC	
	Toluene (µg/L)	Bromo- dichloro- methane (µg/L)	Dichloro- difluoro- methane (µg/L)	Chloro- form (µg/L)	Carbon tetra- chloride (µg/L)	Vinyl chloride (µg/L)	trans- 1,2-Di- chloro- ethene (µg/L)	cis-1,2- Di- chloro- ethene (μg/L)	Tri- chloro- ethene (µg/L)	Tetra- chloro- ethene (µg/L)
SW060H	<1.0	<1.0	< 5.0	6.2	5.4	<1.0	< 2.0	<1.0	<1.0	<1.0
SW060L	<1.0	<1.0	< 5.0	2.7	2.8	<1.0	< 2.0	<1.0	<1.0	<1.0
SW060L	<1.0	<1.0	< 5.0	2.9	3.5	<1.0	<2.0	<1.0	<1.0	<1.0
SW090H	<1.0	<1.0	< 5.0	18.0	9.2	<1.0	< 2.0	<1.0	4.2	3.1
SW090L	<1.0	<1.0	<5.0	15.9	7.7	<1.0	<2.0	<1.0	3.0	3.0
Travel Blank	<1.0	<1.0	<5.0	<1.0	<1.0	<1.0	<2.0	<1.0	<1.0	<1.0
Trip Blank	<1.0	<1.0	<5.0	<1.0	<1.0	<1.0	<2.0	<1.0	<1.0	<1.0
SW010H	<1.0	< .5	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	<1.0
SW015H	<1.0	< .5	<1.0	1.1	< .5	< .5	< .5	< .5	<1.0	<1.0
SW019H	<1.0	< .5	<1.0	1.6	< .5	< .5	< .5	< .5	<1.0	<1.0
SW020H	<1.0	2.31 <b>E</b>	<1.0	9.2	< .5	< .5	< .5	< .5	<1.0	<1.0
SW028H	<1.0	< .5	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	<1.0
SW028M	<1.0	< .5	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	<1.0
SW029H	<1.0	< .5	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	<1.0
SW029M	<1.0	< .5	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	<1.0
SW030H	<1.0	< .5	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	<1.0
SW030H	<1.0	< .5	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	<1.0
SW040H	<1.0	< .5	<1.0	2.5	2.4	< .5	< .5	< .5	<1.0	<1.0
SW040M	<1.0	< .5	<1.0	5.9	6.0	< .5	< .5	< .5	<1.0	<1.0
SW040L	<1.0	< .5	<1.0	3.7	4.4	< .5	< .5	< .5	<1.0	<1.0
SW049L	<1.0	< .5	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	<1.0
SW049L	<1.0	< .5	<1.0	.5	< .5	< .5	< .5	< .5	<1.0	<1.0
SW049.01L	<1.0	< .5	<1.0	1.3	< .5	< .5	< .5	< .5	<1.0	<1.0
SW050H	<1.0	< .5	<1.0	1.3	1.0	< .5	< .5	< .5	<1.0	<1.0
SW050H	<1.0	< .5	<1.0	1.2	1.1	< .5	< .5	< .5	<1.0	<1.0
SW050M	<1.0	< .5	<1.0	4.9	5.1	< .5	< .5	< .5	<1.0	<1.0
SW050L	<1.0	< .5	<1.0	4.7	5.2	< .5	< .5	< .5	<1.0	<1.0
SW050L-MS	spike	< .5	<1.0	4.9	4.7	< .5	< .5	< .5	spike	<1.0
SW050L-MS	spike	< .5	<1.0	5.1	5.0	< .5	< .5	< .5	spike	<1.0
SW060H	<1.0	< .5	<1.0	1.7	1.8	< .5	< .5	< .5	<1.0	<1.0
SW060H	<1.0	< .5	<1.0	1.5	1.4	< .5	< .5	< .5	<1.0	<1.0
SW060M	<1.0	< .5	<1.0	4.6	4.7	< .5	< .5	< .5	<1.0	<1.0
SW060L	<1.0	< .5	<1.0	4.2	4.1	< .5	< .5	< .5	<1.0	<1.0
SW060L-MS	spike	< .5	<1.0	3.6	1.8	< .5	< .5	< .5	spike	<1.0
	spike	< .5	<1.0	4.0	4.0	< .5	< .5	< .5	-r	<1.0

**Appendix B.** Organic constituents in surface-water samples from the Canal Creek area, Aberdeen Proving Ground, Maryland, November 1999 through September 2000—Continued

					FIE	LD PARAMI	ETERS	CHLORINATED ETHANES		
Sample name	Tide	Date collected	Time collected	Replicate number	Specific conduct- ance (µS/cm)	pH (standard units)	Tem- perature (°C)	1,1,2,2- Tetra- chloro- ethane (µg/L)	1,1,2- Trichloro- ethane (µg/L)	1,2- Dichloro- ethane (µg/L)
				May 2000 Sa	ampling Even	ot-Continued				
SW074H	High	05/17/2000	911	na	716	7.6	20.6	<1.0	<1.0	< 0.5
SW074M	Mid	05/17/2000	1158	na	645	7.5	20.8	<1.0	<1.0	< .5
SW074L	Low	05/17/2000	1530	na	533	7.5	25.8	<1.0	<1.0	< .5
SW076H	High	05/17/2000	904	na	719	7.7	20.5	<1.0	<1.0	< .5
SW076M	Mid	05/17/2000	1151		700	7.7	21.5	<1.0	<1.0	< .5
SW076M SW076L	Low	05/17/2000	1525	na na	627	7.5 7.6	24.5	1.4	<1.0	< .5
3WU/0L	Low	03/17/2000	1323	na	027	7.0	24.3	1.4	<1.0	< .5
SW077H	High	05/17/2000	858	na	720	7.7	20.4	<1.0	<1.0	< .5
SW077M	Mid	05/17/2000	1145	na	732	7.6	21.2	<1.0	<1.0	< .5
SW077L	Low	05/17/2000	1516	1	963	7.4	28.7	<1.0	<1.0	< .5
SW077L	Low	05/17/2000	1516	2	-	_	-	<1.0	<1.0	< .5
SW078H	High	05/17/2000	853	na	720	8.0	20.6	<1.0	<1.0	< .5
SW078L	Low	05/17/2000	1512	1	632	7.7	24.2	<1.0	<1.0	< .5
SW078L	Low	05/17/2000	1512	2	-	_	_	<1.0	<1.0	< .5
SW078L SW078M	Mid	05/17/2000	1143	1	708	- 7.6	21.3	<1.0	<1.0	< .5
SW078M			1143	2						
5 W U / 8 W I	Mid	05/17/2000	1143	2	_	_	_	<1.0	<1.0	< .5
SW079H	High	05/17/2000	850	na	716	7.9	20.4	<1.0	<1.0	< .5
SW079M	Mid	05/17/2000	1141	na	700	7.6	21.4	<1.0	<1.0	< .5
SW079L	Low	05/17/2000	1508	1	579	7.6	24.4	1.8	<1.0	< .5
SW079L	Low	05/17/2000	1508	2	_	-	-	2.0	<1.0	< .5
SW080H	High	05/17/2000	847	na	718	7.8	20.6	<1.0	<1.0	< .5
SW080M	Mid	05/17/2000	1134	na	710	7.8	21.3	<1.0	<1.0	< .5
SW080L	Low	05/17/2000	1503	na	638	7.7	24.0	1.6	<1.0	< .5
SW090H	High	05/17/2000	844	20	719	7.9	20.8	<1.0	<1.0	< .5
SW090H SW090M	High Mid	05/17/2000	1131	na	719	7.9 7.9	20.8			
SW090M SW090L				na	712				- 1.0	_ 
SW090L SW090L	Low Low	05/17/2000 05/17/2000	1500 1500	1 2	/12 -	8.0	22.8	<1.0 <1.0	<1.0 <1.0	< .5 < .5
3 W U9UL	Low	03/17/2000	1300	2	_	_	_	<1.0	<1.0	< .5
SW100H	High	05/17/2000	840	1	718	7.5	-	<1.0	<1.0	< .5
SW100H	High	05/17/2000	841	2	_	_	_	<1.0	<1.0	< .5
SW100M	Mid	05/17/2000	1126	na	719	8.6	22.0	<1.0	<1.0	< .5
SW100L	Low	05/17/2000	1455	na	714	8.5	22.7	<1.0	<1.0	< .5
				Field Blank	Samples, Ma	y 2000				
SW020H	_	05/17/2000	946	na	_	_	_	<1.0	<1.0	< .5
SW029H	_	05/17/2000	915	na	_	_	_	<1.0	<1.0	< .5
SW029M	_	05/17/2000	1205	na	_	_	_	<1.0	<1.0	< .5
SW060H	_	05/17/2000	834	na	_	_	_	<1.0	<1.0	< .5
SW060L	_	05/17/2000	1449	na	_	_	_	<1.0	<1.0	< .5
Boat	_	05/17/2000	920	na	_	_	_	<1.0	<1.0	< .5
Boat	-	05/17/2000	-	na	_	_	_	<1.0	<1.0	< .5
F.T. /C :		05/15/2000	026	_	Samples, May	2000		4.0	.1.0	
Van/foot	-	05/17/2000	826	na	_	_	_	<1.0	<1.0	< .5
Boat	_	05/17/2000	_	na	_	_	_	<1.0	<1.0	< .5

	CHL	ORINATED	ETHENES			RINATED THANES		TIONAL VOL		
Tetra- chloro- ethene (µg/L)	Tri- chloro- ethene (µg/L)	cis-1,2- Di- chloro- ethene (μg/L)	trans- 1,2-Di- chloro- ethene (µg/L)	Vinyl chloride (µg/L)	Carbon tetra- chloride (µg/L)	Chloro- form (µg/L)	Dichloro- difluoro- methane (µg/L)	Bromo- dichloro- methane (µg/L)	Toluene (μg/L)	Sample name
<1.0	<1.0	< 0.5	< 0.5	< 0.5	2.2	2.2	<1.0	< 0.5	<1.0	SW074H
<1.0	<1.0	< .5	< .5	< .5	4.7	5.2	<1.0	< .5	<1.0	SW074M
<1.0	<1.0	< .5	< .5	< .5	2.0	2.7	<1.0	< .5	<1.0	SW074L
<1.0	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	< .5	<1.0	SW076H
<1.0	<1.0	< .5	< .5	< .5	3.3	3.2	<1.0	< .5	<1.0	SW076M
1.1	<1.0	< .5	< .5	< .5	6.6	7.5	<1.0	< .5	<1.0	SW076L
<1.0	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	< .5	<1.0	SW077H
<1.0	<1.0	< .5	< .5	< .5	< .5	.9	<1.0	< .5	<1.0	SW077M
<1.0	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	< .5	<1.0	SW077L
<1.0	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	< .5	<1.0	SW077L
<1.0	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	< .5	<1.0	SW078H
<1.0	<1.0	< .5	< .5	< .5	5.3	6.4	<1.0	< .5	<1.0	SW078L
<1.0	<1.0	< .5	< .5	< .5	4.7	5.7	<1.0	< .5	<1.0	SW078L
<1.0	<1.0	< .5	< .5	< .5	2.6	2.6	<1.0	< .5	<1.0	SW078M
<1.0	<1.0	< .5	< .5	< .5	2.2	2.3	<1.0	< .5	<1.0	SW078M
<1.0	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	< .5	<1.0	SW079H
<1.0	<1.0	< .5	< .5	< .5	1.1	1.5	<1.0	< .5	<1.0	SW079M
<1.0	<1.0	< .5	< .5	< .5	< .5	1.6	<1.0	< .5	<1.0	SW079L
<1.0	1.0	.9	< .5	< .5	1.4	1.9	<1.0	< .5	<1.0	SW079L
<1.0	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	< .5	<1.0	SW080H
<1.0	<1.0	< .5	< .5	< .5	< .5	1.0	<1.0	< .5	<1.0	SW080M
<1.0	<1.0	.8	< .5	< .5	2.6	3.2	<1.0	< .5	<1.0	SW080L
<1.0	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	< .5	<1.0	SW090H
_	_	_	_	_	_	_	_	_	_	SW090M
<1.0	<1.0	< .5	< .5	< .5	1.6	2.1	<1.0	< .5	<1.0	SW090L
<1.0	<1.0	< .5	< .5	< .5	2.1	2.2	<1.0	< .5	<1.0	SW090L
<1.0	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	< .5	<1.0	SW100H
<1.0	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	< .5	<1.0	SW100H
<1.0	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	< .5	<1.0	SW100M
<1.0	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	< .5	<1.0	SW100L
<1.0	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	< .5	<1.0	SW020H
<1.0	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	< .5	<1.0	SW029H
<1.0	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	< .5	<1.0	SW029M
<1.0	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	< .5	<1.0	SW060H
<1.0	<1.0	< .5	< .5	< .5	< .5	< .5	<1.0	< .5	<1.0	SW060L
<1.0 <1.0	<1.0 <1.0	< .5 < .5	< .5 < .5	< .5 < .5	< .5 < .5	< .5 < .5	<1.0 <1.0	< .5 < .5	<1.0 <1.0	Boat Boat
<1.0	<1.0	< .5	< .5	< .3	< .5	< .5	<1.0	< .5	<1.0	Doai
1.0		_	_	_	_	_	1.0	_	1.6	<b>T.</b> (C
<1.0	<1.0	< .5 < .5	< .5 < .5	< .5 < .5	< .5 < .5	< .5 < .5	<1.0 <1.0	< .5 < .5	<1.0 <1.0	Van/foot Boat
<1.0	<1.0									

**Appendix B.** Organic constituents in surface-water samples from the Canal Creek area, Aberdeen Proving Ground, Maryland, November 1999 through September 2000—Continued

					FIE	LD PARAMI	ETERS	CHL	ORINATED E	THANES
Sample name	Tide	de Date collected	Time collected	Replicate number	Specific conduct- ance (µS/cm)	pH (standard units)	Tem- perature (°C)	1,1,2,2- Tetra- chloro- ethane (µg/L)	1,1,2- Trichloro- ethane (µg/L)	1,2- Dichloro- ethane (µg/L)
				September 2	2000 Sampling	g Event				
SW020H	High	09/14/2000	1022	na	188	9.6	22.8	< 0.5	<1.0	< 0.5
SW020L	Low	09/14/2000	1645	na	325	10.1	27.0	< .5	<1.0	< .5
SW030H	High	09/14/2000	1007	1	214	7.1	19.2	< .5	<1.0	< .5
SW030H	High	09/14/2000	1007	2	_	_	_	< .5	<1.0	< .5
SW030L	Low	09/14/2000	1635	na	220	7.4	22.3	< .5	<1.0	< .5
SW049H	High	09/14/2000	1015	1	1,600	5.6	_	3.1	<1.0	< .5
SW049H	High	09/14/2000	1015	2	-	-	_	3.4	<1.0	< .5
SW049M	Mid	09/14/2000	1322	1	1,550	7.0	_	1.8	<1.0	< .5
SW049M	Mid	09/14/2000	1322	2	-	_	_	2.1	<1.0	< .5
SW049L	Low	09/14/2000	1630	1	_	_	_	1.8	<1.0	< .5
SW049L*	Low	09/14/2000	1630	2	640	6.6	_	1.5	<1.0	< .5
SW049.01H	High	09/14/2000	1025	1	1,370	6.6	_	3.0	<1.0	< .5
SW049.01H	High	09/14/2000	1025	2	_	_	_	3.4	<1.0	< .5
SW049.01M	Mid	09/14/2000	1330	1	1,440	6.9	_	1.5	<1.0	< .5
SW049.01M	Mid	09/14/2000	1330	2	_	_	_	1.4	<1.0	< .5
SW049.01L	Low	09/14/2000	1635	1	1,650	6.3	_	< .5	<1.0	< .5
SW049.01L	Low	09/14/2000	1635	2	_	_	_	< .6	<1.1	< .6
SW049.01L	Low	9/13/2000	1635	3	-	_	-	< .5	<1.0	< .5
SW060H	High	09/14/2000	1010	na	3,420	6.5	_	.8	<1.0	< .5
SW060M	Mid	09/14/2000	1315	na	2,030	7.0	_	1.9	<1.0	< .5
SW060L	Low	09/14/2000	1620	na	1,100	6.9	-	6.6	<1.0	< .5
SW090H	High	09/14/2000	950	1	6,360	7.2	23.7	< .5	<1.0	< .5
SW090H	High	09/14/2000	950	2	_	_	_	< .5	<1.0	< .5
SW090M	Mid	09/14/2000	1320	1	6,030	7.6	25.8	< .5	<1.0	< .5
SW090M	Mid	09/14/2000	1320	2	_	_	_	< .5	<1.0	< .5
SW090L	Low	09/14/2000	1620	1	6,260		8.7	28.2	<1.0	< .5
SW090L	Low	09/14/2000	1620	2	-	-	-	< .5	<1.0	< .5
				2000 Hover	orobe Samplii	ng Events				
SWHP01	_	09/11/2000	1250	1	_	-	-	1.3	<1.0	< .5
SWHP01	_	09/11/2000	1250	2	_	-	-	1.4	<1.0	< .5
SWHP02	_	09/11/2000	1030	1	_	-	_	< .5	<1.0	< .5
SWHP02	_	09/11/2000	1030	2	_	-	-	< .5	<1.0	< .5
SWHP05	-	09/11/2000	1000	1	_	-	-	< .5	<1.0	< .5
SWHP05	-	09/11/2000	1000	2	_	_	_	< .5	<1.0	< .5
SWHP07	_	03/13/2000	_	1	_	_	_	3.6	< .5	< .5
SWHP08	_	03/13/2000	_	1	_	-	_	1.4	< .5	< .5
SWHP09	-	03/14/2000	-	1	-	-	-	3.6	< .5	< .5
SWHP13	-	09/11/2000	1440	1	-	-	-	2.4	<1.0	< .5
SWHP13	_	09/11/2000	1440	2	_	_	_	2.5	<1.0	< .5

	CHL	ORINATED	ETHENES			RINATED THANES		TIONAL VOL		
Tetra- chloro- ethene (µg/L)	Tri- chloro- ethene (µg/L)	cis-1,2- Di- chloro- ethene (μg/L)	trans- 1,2-Di- chloro- ethene (µg/L)	Vinyl chloride (µg/L)	Carbon tetra- chloride (µg/L)	Chloro- form (µg/L)	Dichloro- difluoro- methane (µg/L)	Bromo- dichloro- methane (µg/L)	Toluene (μg/L)	Sample name
< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1.7	< 5.0	< 0.5	< 0.5	SW020H
< .5	< .5	< .5	< .5	< .5	< .5	1.2	< 5.0	< .5	< .5	SW020L
< .5	< .5	< .5	< .5	< .5	< .5	< .5	< 5.0	< .5	< .5	SW030H
< .5	< .5	< .5	< .5	< .5	< .5	< .5	< 5.0	< .5	< .5	SW030H
< .5	< .5	< .5	< .5	< .5	< .5	< .5	< 5.0	< .5	< .5	SW030L
1.5	.8	< .5	< .5	< .5	9.0	11.2	<5.0	< .5	< .5	SW049H
1.3	.8 .9	< .5	< .5	< .5 < .5	9.0 8.4	11.2	<5.0 <5.0	< .5	< .5 < .5	SW049H SW049H
										SW049H SW049M
1.0 .9	< .5 < .5	< .5 < .5	< .5 < .5	< .5 < .5	4.5 4.4	6.0 5.9	<5.0 <5.0	< .5 < .5	< .5 < .5	SW049M SW049M
< .5	1.1 1.8	3.7	1.2	< .5	< .5	.8	<5.0	< .5	< .5	SW049L SW049L*
< .5	1.8	5.3	7.1	33.3	< .5	< .5	9.8	< .5	.7	SW049L*
1.6	.6	< .5	< .5	< .5	9.0	11.1	< 5.0	< .5	< .5	SW049.01H
1.4	.7	< .5	< .5	< .5	7.7	9.7	< 5.0	< .5	< .5	SW049.01H
< .5	< .5	< .5	< .5	< .5	1.8	3.9	< 5.0	< .5	< .5	SW049.01M
< .5	< .5	< .5	< .5	< .5	1.9	3.9	< 5.0	< .5	< .5	SW049.01M
< .5	< .5	< .5	< .5	< .5	< .5	< .5	< 5.0	< .5	< .5	SW049.01L
< .6	< .6	< .6	< .6	< .6	< .6	< .6	< 5.0	< .6	< .6	SW049.01L
< .5	< .5	< .5	< .5	< .5	< .5	< .5	< 5.0	< .5	< .5	SW049.01L
1.0	< .5	< .5	< .5	< .5	4.8	6.0	<5.0	< .5	< .5	SW060H
1.4	.5	< .5	< .5	< .5	7.3	8.7	<5.0	< .5	< .5	SW060M
.8	.8	< .5	< .5	< .5	6.3	5.1	< 5.0	< .5	< .5	SW060L
< .5	< .5	< .5	< .5	< .5	< .5	< .5	<5.0	< .5	< .5	SW090H
< .5 < .5	< .5 < .5	< .5	< .5	< .5 < .5	< .5	< .5	<5.0 <5.0	< .5	< .5 < .5	SW090H SW090H
< .5	< .5	< .5	< .5	< .5	< .5	< .5	<5.0	< .5	< .5	SW090M
< .5	< .5	< .5	< .5	< .5	< .5	< .5	<5.0	< .5	< .5	SW090M SW090M
< .5	< .5	< .5	< .5	< .5	< .5	< .5	<5.0	< .5	< .5	SW090L
< .5	< .5	< .5	< .5	< .5	< .5	< .5	<5.0	< .5	< .5	SW090L
1.1	< .5	< .5	< .5	< .5	4.8	6.2	< .5	< .5	< .5	SWHP01
1.0	< .5	< .5	< .5	< .5	4.9	6.3	< .5	< .5	< .5	SWHP01
< .5	< .5	< .5	< .5	< .5	1.3	1.6	< .5	< .5	< .5	SWHP02
< .5	< .5	< .5	< .5	< .5	1.2	1.7	< .5	< .5	< .5	SWHP02
.7	< .5	< .5	< .5	< .5	2.3	3.5	< .5	< .5	< .5	SWHP05
< .5	< .5	< .5	< .5	< .5	2.4	3.5	< .5	< .5	< .5	SWHP05
1.4	1.4	< .5	< .5	< .5	7.5	9.3	< .5	< .5	<10.0	SWHP07
< .5	< .5	< .5	< .5	< .5 < .5	2.5	9.3 4.0	< .5 < .5	< .5	<10.0	SWHP08
< .5 2.9	< .5 1.8	< .3 .8	< .5 < .5	< .5 < .5	2.5 16.0	4.0 15.9	< .5 < .5	< .5 < .5	<10.0	SWHP09
1.4	< .5	< .5	< .5	< .5	6.1	7.6	< .5 < .5	< .5	< .5	SWHP13
1.4	< .5 < .5	< .5	< .5		6.2	7.8	< .5 < .5	< .5 < .5	< .5 < .5	SWHP13
1.3	< .3	< .3	< .5	< .5	0.2	1.8	< .3	< .5	< .5	SWUL12