



Assessment of Volatile Organic Compounds
in Surface Water
at West Branch Canal Creek,
Aberdeen Proving Ground, Maryland,
1999



2000
Aberdeen Proving Ground, Edgewood Area

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Assessment of Volatile Organic Compounds in in Surface Water at West Branch Canal Creek, Aberdeen Proving Ground, Maryland, 1999

By Lisa D. Olsen and Tracey A. Spencer

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

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For additional information contact:

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

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CONVERSION FACTORS, ABBREVIATIONS, AND VERTICAL DATUM

Multiply	By	To obtain
inch (in.)	2.54	Centimeter
foot (ft)	0.3048	Meter
mile (mi)	1.609	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: Concentrations of chemical constituents in water are expressed in micrograms per liter ($\mu\text{g/L}$).

ASSESSMENT OF VOLATILE ORGANIC COMPOUNDS IN SURFACE WATER AT WEST BRANCH CANAL CREEK, ABERDEEN PROVING GROUND, MARYLAND, 1999

By Lisa D. Olsen and Tracey A. Spencer

ABSTRACT

The U.S. Geological Survey (USGS) collected 13 surface-water samples and 3 replicates from 5 sites in the West Branch Canal Creek area at Aberdeen Proving Ground from February through August 1999, as a part of an investigation of ground-water contamination and natural attenuation processes. The samples were analyzed for volatile organic compounds, including trichloroethylene, 1,1,2,2-tetrachloroethane, carbon tetrachloride, and chloroform, which are the four major contaminants that were detected in ground water in the Canal Creek area in earlier USGS studies. Field blanks were collected during the sampling period to assess sample bias. Field replicates were used to assess sample variability, which was expressed as relative percent difference. The mean variability of the surface-water replicate analyses was larger (35.4 percent) than the mean variability of ground-water replicate analyses (14.6 percent) determined for West Branch Canal Creek from 1995 through 1996. The higher variability in surface-water analyses is probably due to heterogeneities in the composition of the surface water rather than differences in sampling or analytical procedures. The most frequently detected volatile organic compound was 1,1,2,2-tetrachloroethane, which was detected in every sample and in two of the replicates. The surface-water contamination is likely the result of cross-media transfer of contaminants from the ground water and sediments along the West Branch Canal Creek. The full extent of surface-water contamination in West Branch Canal Creek and the locations of probable contaminant sources cannot be determined from this limited set of data. Tidal mixing, creek flow patterns, and potential effects of a drought that occurred during the sampling period also complicate the evaluation of surface-water contamination.

INTRODUCTION

Samples of surface water were collected in the West Branch Canal Creek area of Aberdeen Proving Ground (APG), Maryland (fig. 1), from February through August 1999 to

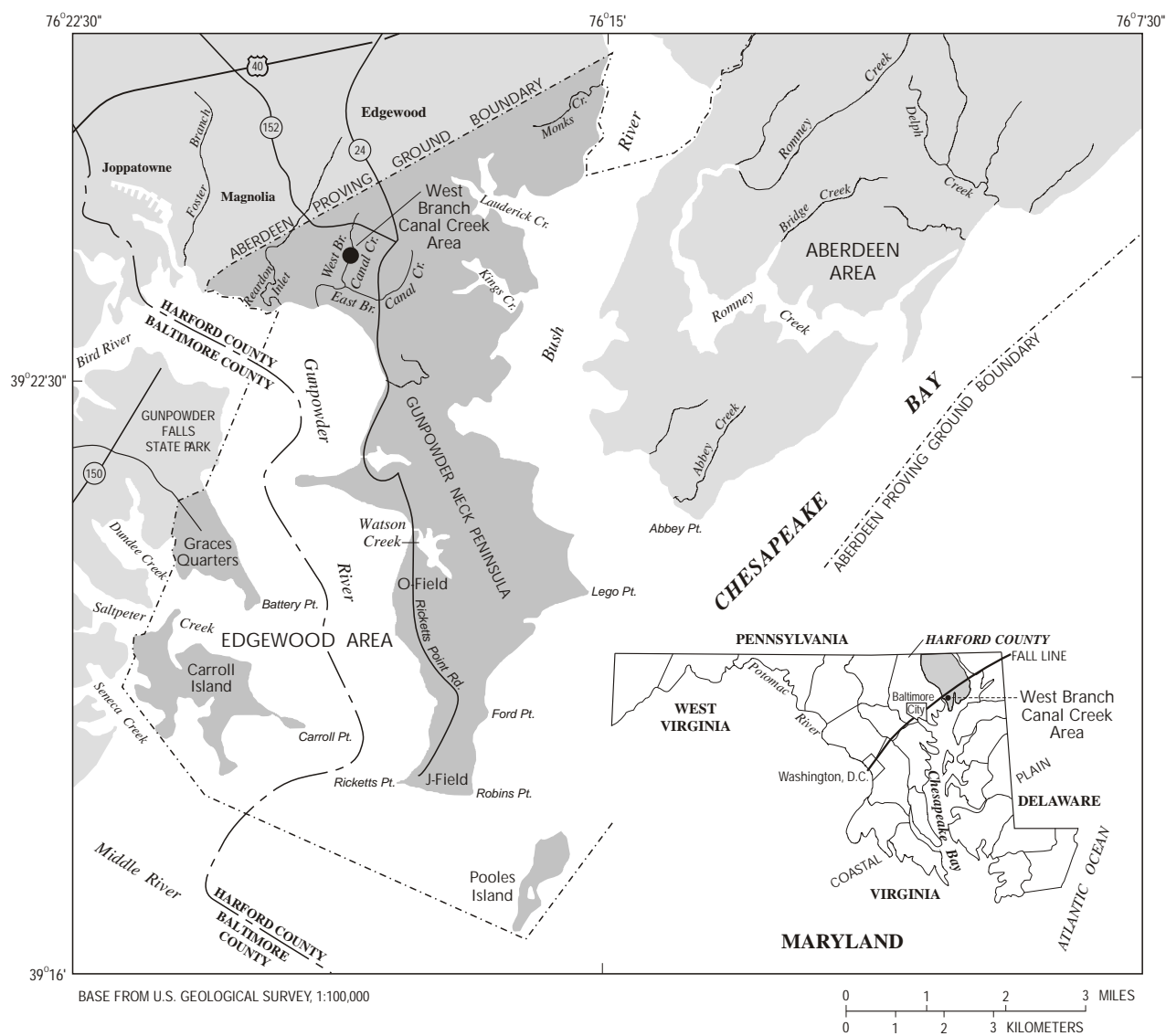


Figure 1. Location of West Branch Canal Creek area, Aberdeen Proving Ground, Maryland (modified from Lorah and Clark, 1996).

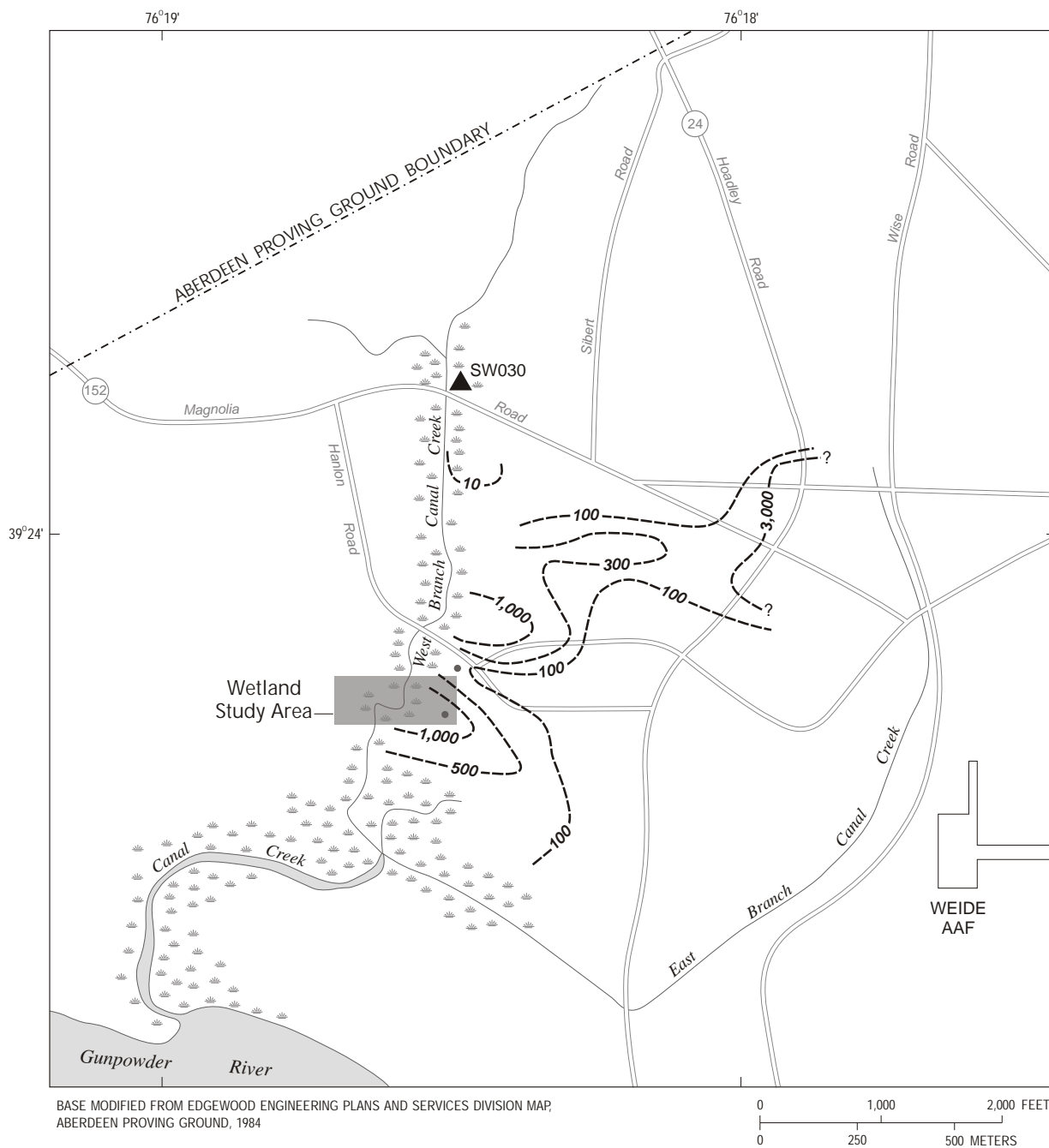
assess the presence and distribution of volatile organic compounds (VOCs). Although the focus of the current USGS investigation is to determine the extent of ground-water contamination in the West Branch Canal Creek area and the role of natural attenuation processes in the wetland sediments, some natural attenuation processes may result in the transfer of contaminants from one media to another, such as from ground water to surface water (U.S. Environmental Protection Agency, 1999). Surface-water samples were collected to determine whether cross-media transfer of VOCs from ground water to the overlying surface water could be occurring in the West Branch Canal Creek area.

Purpose and Scope

The purpose of this report is to provide information about VOC contamination detected in surface-water samples collected by the USGS in the West Branch Canal Creek area from February through August 1999. The report presents the VOC data from these samples and an evaluation of the corresponding quality-assurance data. It does not address potential risks from VOCs in surface water at the concentrations detected or processes that are likely to affect VOC fate and transport in surface water, such as volatilization. This report also discusses the likelihood of localized transfer of VOCs to surface water from ground-water sources, but does not identify specific locations at which such contaminant transfer may be occurring. Although sample collection was limited to a stretch of the West Branch Canal Creek between the USGS stream-gaging station at Magnolia Road and the southern boundary of the wetland study area (fig. 2), the results of this assessment of VOCs in surface water may have implications for other areas of Canal Creek.

Location of Surface-Water Sampling Sites

Surface-water samples were collected at five sites. Site SW030 is on West Branch Canal Creek at Magnolia Road near a USGS stream-gaging station (fig. 2). Site SW030 is upgradient of the point at which the creek becomes tidally influenced; however, this site has been known to receive tidal backwash during extreme weather events (D. J. Phelan, U.S. Geological Survey, oral commun., 1999). The other four sampling sites are within the wetland study area, approximately 2,500 ft (feet) south (downstream) of site SW030, and are



EXPLANATION

- ?--10-- APPROXIMATE LINE OF EQUAL TOTAL ORGANIC HALOGEN CONCENTRATION -- Interval, in micrograms per liter, is variable. Queried where uncertain. Sampled in July-September 1988.
- SW030 ▲ STREAM-GAGE AND SURFACE-WATER SITE AND IDENTIFICATION NUMBER

Figure 2. Location of surface-water sampling site SW030 and the wetland study area along the West Branch Canal Creek, Aberdeen Proving Ground, Maryland, and the distribution of total organic halogen in the Canal Creek aquifer upgradient from the wetland (modified from Lorah and Clark, 1996, p. 106).

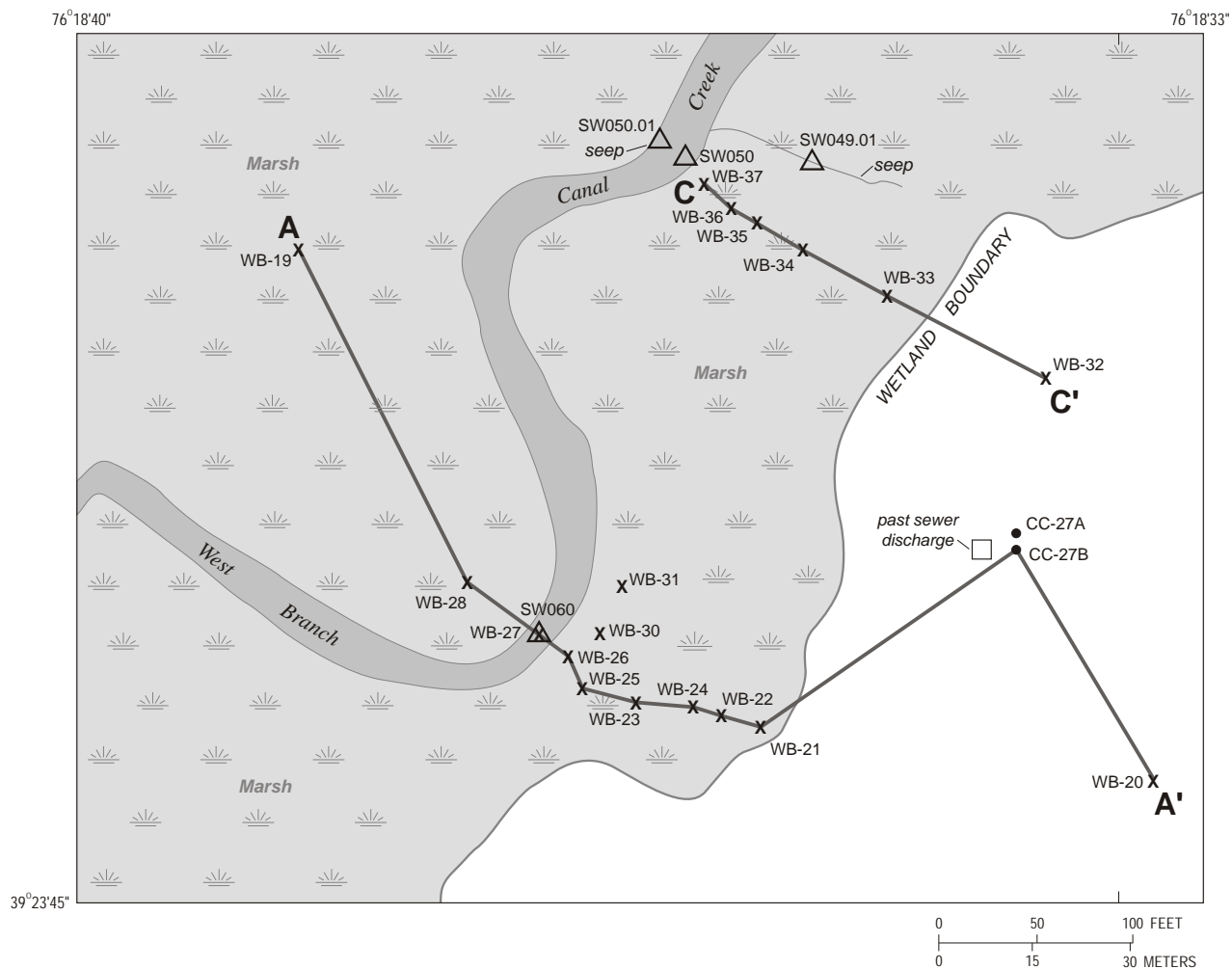
tidally influenced. Locations of these sites are shown in figure 3. Site SW049.01 is within a seep that frequently appears at low tide, north of transect C-C' in the wetland study area. Site SW050 is at West Branch Canal Creek at the west end of the walkway on transect C-C'. Site SW050.01 is within a seep that appeared at low tide in March 1999, on the west side of the creek, opposite the walkway at the end of transect C-C'. Unlike surface water collected at the other sampling sites, the water in this seep was black. Site SW060 is at West Branch Canal Creek at the walkway bridge on transect A-A'. Site numbers increase in the downstream direction; for example, SW060 is downstream of SW050.

Acknowledgments

The authors thank John Wrobel of the U.S. Army Environmental Conservation and Restoration Division, APG, for his assistance and support of this investigation. We thank Peter Pritchard and his crew from the Aberdeen Test Center, APG, for providing logistical support, including the installation of walkways and a bridge in the wetland study area. We thank Alan Rosencrance of the U.S. Army Center for Environmental Health Research, Fort Detrick, Maryland, for providing the on-site laboratory trailer and support associated with its operation. The authors also wish to acknowledge the following USGS personnel in the Maryland-Delaware-D.C. District who assisted in collection of water-quality data for this investigation—Mastin Mount, Michelle Lorah, Daniel Phelan, Linda Jo Dyer, Julie Kirshtein, and Jonathan Johnson.

METHODS OF INVESTIGATION

Surface-water samples were collected at each creek site by dipping a sample vial 3 to 5 in.(inches) below the water surface and then capping each vial as quickly as possible to limit sample aeration and VOC losses due to volatilization. Samples from the seep sites were collected by submerging the vials as deeply as possible without disturbing the sediments, sometimes only 1 in. or less below the water surface. Samples were typically collected at low tide, or at times when the water level in the creek was relatively low, to minimize the proportion of tidal backwash in the creek. Wind, precipitation patterns, ice, and other weather events in the Gunpowder River and the Chesapeake Bay area can dramatically affect the water levels in the West Branch Canal Creek, so the water levels are not always consistent with the lunar tidal cycle.



EXPLANATION

CC-27A ● 4-INCH WELL FROM PREVIOUS STUDY AND IDENTIFICATION NUMBER

WB-20 x 0.75-INCH PIEZOMETER SITE FROM PREVIOUS STUDY AND IDENTIFICATION NUMBER

A-A' LINE OF SECTION

SW060 △ SURFACE-WATER SITE AND IDENTIFICATION NUMBER

Figure 3. Locations of additional surface-water sampling sites within the wetland study area along the West Branch Canal Creek, Aberdeen Proving Ground, Maryland (modified from Lorah and others, 1997, p. 8).

Samples were placed on ice and carried to an on-site laboratory, where they were refrigerated prior to analysis. Samples were analyzed within 14 days of collection for VOC's by purge and trap gas chromatography with a mass-selective detector. The analytical method is based upon U.S. Environmental Protection Agency Method 524.2 and is described in Rose and Schroeder (1995).

VOLATILE ORGANIC COMPOUND DATA

The surface-water-quality data for selected VOCs at the West Branch Canal Creek area are presented in table 1. All concentrations and quality-assurance data were reviewed by the Analyst and verified by the Project Chief. The data are grouped by chemical structure and are listed in order of decreasing degree of chlorination so that parent compounds are generally listed before possible biodegradation daughter products. Reporting limits varied between 0.5 and 2.0 µg/L (micrograms per liter) due to matrix interferences and periodic variations in instrument performance. Reporting limits were determined and verified through repeated analysis of calibration standards. Concentrations were rounded to the nearest 0.1 µg/L.

QUALITY-ASSURANCE DATA

Quality-assurance samples were collected to evaluate bias and variability in the VOC concentration data. Bias is systematic error that may result from contaminants being introduced into a sample or analytes being lost from a sample during collection, processing, or analysis. Variability is random error in independent measurements of the same quantity, and may result from variations in sampling and analytical procedures. For environmental samples and their replicates, intrinsic heterogeneities in the quantity that is being measured (in this case, VOCs in surface water) are also a source of variability.

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 described 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 that report.

Bias and variability also were evaluated by use of field blanks and field replicates. Field blanks and field replicates integrated sources of bias and variability from all steps of the sample-collection, processing, and analysis procedures.

Table 1. Results of analyses of surface-water samples for selected volatile organic compounds (VOCs); West Branch Canal Creek area, Aberdeen Proving Ground, Maryland--February through August 1999

[Water levels in feet above sea level; µg/L; micrograms per liter; <, less than; na, not applicable; --, no data]

Site number	Repl-icate	Date collected	Time	Tide level	Water level	Report- ing limit (µg/L)	Chlorinated Ethanes		
							1,1,2,2- Tetra- chloro- ethane (µg/L)	1,1,2- Tri- chloro- ethane (µg/L)	1,2-Di- chloro- ethane (µg/L)
SW030	na	07-29-1999	13:30	mid	3.45	0.5	3.0	< 0.5	< 0.5
SW030	na	07-29-1999	15:30	high	3.90	1.0	1.4	< 1.0	< 1.0
SW049.01	na	02-18-1999	9:30	low	0.86	0.5	18.5	1.9	0.6
SW049.01	1	05-27-1999	10:30	low	3.90	2.0	3.2	< 2.0	< 2.0
SW049.01	2	05-27-1999	10:30	low	3.90	2.0	< 2.0	< 2.0	< 2.0
SW050	na	03-05-1999	12:24	mid	0.19	0.5	6.4	0.9	< 0.5
SW050	na	03-16-1999	--	--	--	0.5	8.3	<0.5	< 0.5
SW050	1	05-27-1999	10:15	low	3.90	2.0	8.5	< 2.0	< 2.0
SW050	2	05-27-1999	10:15	low	3.90	2.0	7.8	< 2.0	< 2.0
SW050.01	na	03-08-1999	10:48	low	0.30	0.5	1.4	1.0	2.2
SW060	na	03-08-1999	10:36	low	0.30	0.5	7.9	0.9	< 0.5
SW060	na	03-16-1999	--	--	--	0.5	7.8	< 0.5	< 0.5
SW060	1	07-23-1999	11:41	low	4.13	0.5	1.0	1.2	< 0.5
SW060	2	07-23-1999	11:41	low	4.13	0.5	3.8	1.2	< 0.5
SW060	na	07-23-1999	13:30	mid	4.18	0.5	2.8	1.0	< 0.5
SW060	na	08-03-1999	9:42	high	3.74	0.5	1.5	< 0.5	< 0.5

Chlorinated Ethenes					Chlorinated Methanes		Additional Compound	Site number
Tetra-chloro-ethene (µg/L)	Tri-chloro-ethene (µg/L)	<i>cis</i> -1,2-Dichloro-ethene (µg/L)	<i>trans</i> -1,2-Dichloro-ethene (µg/L)	Vinyl chloride (µg/L)	Carbon tetra-chloride (µg/L)	Chloro-form (µg/L)	Bromo-methane (µg/L)	
< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	4.3	5.7	< 0.5	SW030
1.3	< 1.0	< 1.0	< 1.0	< 1.0	3.8	5.0	< 1.0	SW030
< 0.5	1.2	2.0	1.2	0.7	0.6	<0.5	0.9	SW049.01
< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	SW049.01
< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	SW049.01
1.0	1.7	< 0.5	< 0.5	< 0.5	6.4	4.0	1.1	SW050
1.1	1.3	< 0.5	< 0.5	< 0.5	5.2	4.1	1.3	SW050
< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	3.0	3.1	< 2.0	SW050
< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	3.8	3.3	< 2.0	SW050
< 0.5	0.7	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1.1	SW050.01
1.1	0.7	< 0.5	< 0.5	< 0.5	6.3	3.1	1.2	SW060
1.5	1.2	< 0.5	< 0.5	< 0.5	6.4	6.9	1.5	SW060
< 0.5	2.4	< 0.5	< 0.5	< 0.5	2.9	2.5	< 0.5	SW060
< 0.5	0.6	< 0.5	< 0.5	< 0.5	2.9	2.3	< 0.5	SW060
< 0.5	1.4	< 0.5	< 0.5	< 0.5	3.5	3.1	< 0.5	SW060
4.2	< 0.5	< 0.5	< 0.5	< 0.5	21.9	22.1	< 0.5	SW060

Field Blanks

Field blanks are typically collected by passing water that is free of the analytes of interest through the equipment that is typically used to collect the environmental samples. In this case, no equipment was used to collect the surface-water samples. The vials were filled and capped while submerged in the surface water that was being sampled. The samples were carried by hand to the laboratory. The sources of contamination bias were therefore limited to the sample vial itself. To conserve analytical resources, six field blanks that were collected for analysis of VOCs between February and August 1999 for an ongoing ground-water tracer test were used to evaluate potential contamination bias in the surface-water samples. These field blanks were collected by using a glass syringe and Teflon tubing to fill the sample vials in the field to overflowing with organic-free water and then quickly capping the vials. No VOCs were detected in these blanks; therefore, contaminant bias in the surface-water samples is considered to be insignificant.

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 sample collected for a particular location and time is designated by a “1” in the “Replicate” column in table 1. If a second sample, or replicate, was collected immediately after the first sample, it is designated by a “2” in the “Replicate” column in table 1. 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. Variabilities were calculated prior to rounding the concentration data, using the following formula:

$$RPD = \frac{|C_1 - C_2|}{(C_1 + C_2) / 2} \times 100 \text{ percent}, \quad (1)$$

where:

RPD is the relative percent difference, and

C₁ and C₂ are the concentrations of the VOC of interest in the replicate samples.

Sources of variability in measured concentrations of VOCs in replicate samples include variations in the sampling procedure and the analytical method, and heterogeneities in the surface-water composition. Surface-water samples may exhibit higher variability for VOCs than ground-water samples because creek water may be unevenly mixed, and because the VOCs in surface water exposed to the atmosphere may rapidly volatilize.

Variability (expressed as RPD) in the results of analyses of VOCs in replicate surface-water samples averaged 13.1 percent for the three analytes detected in samples collected from site SW050 on May 27, 1999, and 48.8 percent for the five analytes detected in samples collected from SW060 on July 23, 1999. The replicate sample pair collected at SW049.01 on May 27, 1999, could not be used to evaluate variability because only one analyte was detected, and that analyte was found in only one of the two samples. The mean RPD for the eight analyses for which RPDs could be calculated was 35.4 percent; however, the median RPD was only 8.7 percent. By comparison, analyses of replicate ground-water samples for VOCs at the on-site laboratory from 1995 through 1996 yielded a mean RPD of 14.6 percent and a median of 9.3 percent (Olsen and others, 1997). The higher mean variability in the surface-water replicates is mainly due to 1,1,2,2-tetrachloroethane (RPD = 114.7 percent) and trichloroethylene (RPD = 114.4 percent) detected at SW060 on July 23, 1999. The remaining six surface-water replicate analyses were similar in variability to ground-water samples analyzed at the on-site laboratory and at the USGS National Water-Quality Laboratory from 1995 through 1996 (fig. 4). Because the variability associated with sampling or analytical procedures tends to affect all of the VOCs in a sample to some degree, the high RPDs for 1,1,2,2-tetrachloroethane and trichloroethylene in the replicate samples from SW060 (collected on July 23, 1999) are far more likely to be caused by natural heterogeneities in the surface-water composition than from sampling or analytical procedures.

ASSESSMENT OF VOLATILE ORGANIC COMPOUNDS IN SURFACE WATER

Concentrations of VOCs in surface-water samples ranged from below the reporting limit to a maximum of 22.1 µg/L for chloroform detected at site SW060 on August 3, 1999 (table 1). The next highest measured concentration was 21.9 µg/L for carbon tetrachloride, detected at site SW060 on August 3, 1999.

At least one VOC was detected in all 13 samples and in 2 of the 3 replicates. Three or more VOCs were detected in 12 of the samples and in 2 replicates. The most frequently

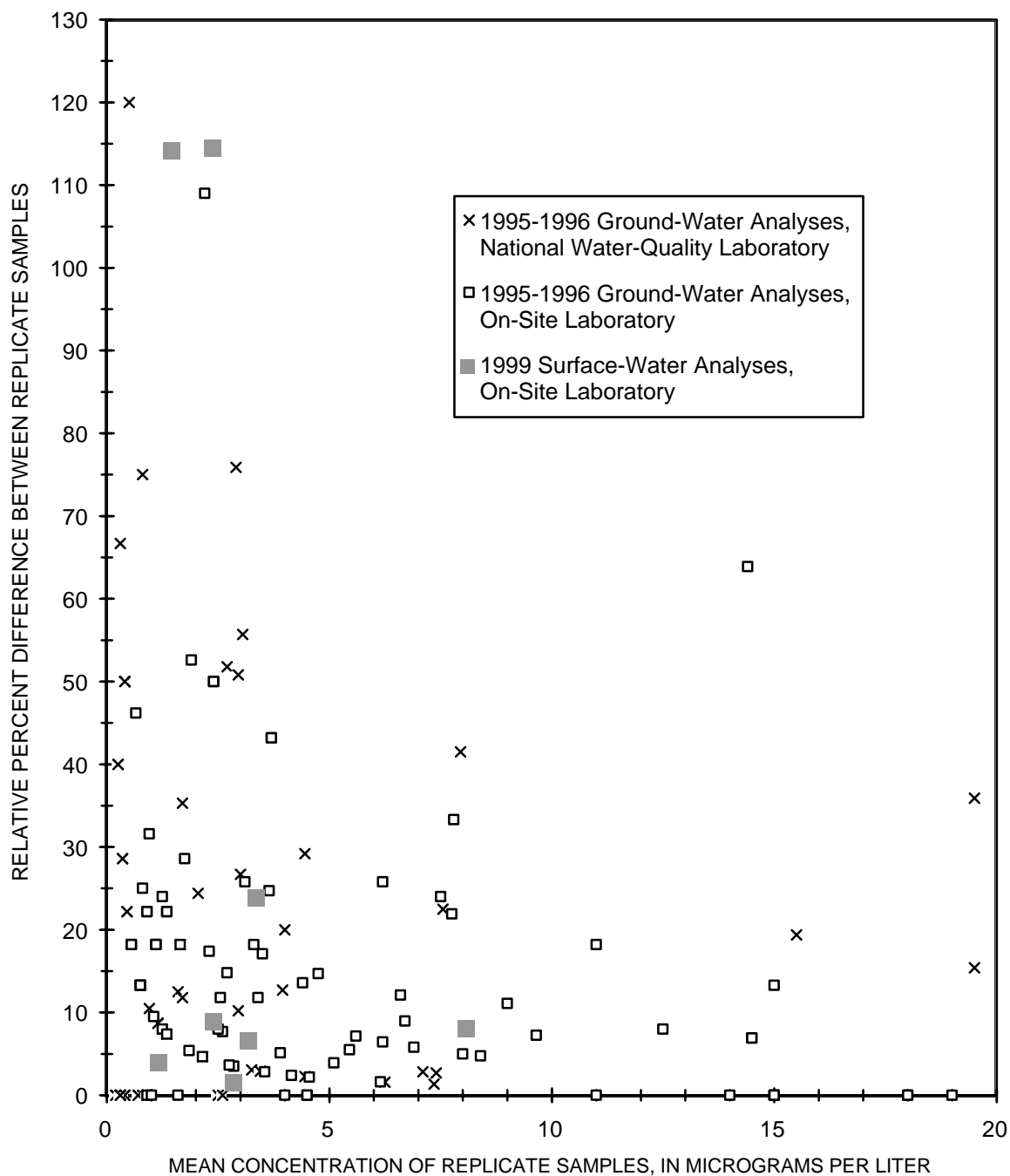


Figure 4. Relative percent differences and mean concentrations of volatile organic analytes in replicate sample pairs (1995-1996 data from Olsen and others, 1997).

detected VOC was 1,1,2,2-tetrachloroethane, which was detected in all of the samples and in two of the replicates. The highest measured concentration of 1,1,2,2-tetrachloroethane was 18.5 µg/L, which was detected at site SW049.01 on February 18, 1999 (table 1). The next most frequently detected VOC was carbon tetrachloride, which was detected in 11 samples and 2 replicates, followed by chloroform, which was detected in 10 samples and 2 replicates. The high frequency of VOC detections in surface-water samples that were collected over the period of about six months and from five different locations indicates that surface-water contamination in West Branch Canal Creek may be a widespread and ongoing problem.

The concentrations of VOCs in samples from sites SW049.01 and SW050.01 (fig. 3) show that ephemeral seeps that discharge water from areas of known contaminant plumes are an intermittent source of VOCs to West Branch Canal Creek. Below-normal rainfall in the winter, spring, and summer of 1999 likely reduced the relative contributions of overland flow (direct runoff) and shallow ground-water discharge to the creek. As a result, base flow in the creek probably consisted mainly of relatively deeper and older ground water that may have been contaminated. Additional surface-water sampling and an evaluation of historical rainfall and hydrologic data would be necessary to determine whether the concentrations of VOCs measured in surface water from February 1999 through August 1999 are typical of West Branch Canal Creek, or whether they were elevated due to the effects of the unusual drought event.

Although ground-water seeps in areas of contaminant plumes in the wetland study area are one likely source of VOC contamination to the creek, the concentrations of VOCs measured at site SW030 (at Magnolia Road) suggest that additional sources of VOCs could be present upstream of the wetland study area (fig. 2). Although tidal inflow during extreme high tides or water levels associated with storms in the Gunpowder River or Chesapeake Bay areas could have carried contaminated water upstream from the wetland study area to SW030, such events are rare and would not provide a long-term source of VOCs, and therefore cannot explain the VOCs measured at SW030 on July 29, 1999. No extreme high tides or storms were associated with this sampling date.

Extensive tidal mixing occurs at sites SW049.01, SW050, SW050.01, and SW060, which are substantially downstream of site SW030. The VOCs detected in samples from these sites may have been the result of contaminated water transported from areas even further downstream. Surface-water samples collected at low tide would be expected to contain a lower proportion of tidal backwash than samples collected at high tide. Additional surface-water sampling could be conducted at both high tide and low tide to determine the distribution of VOCs along the West Branch Canal Creek at both extremes of the tidal cycle,

and to determine the degree to which tidal mixing mitigates or intensifies the concentrations of VOCs in the creek.

SUMMARY AND CONCLUSIONS

Volatile organic compounds were detected in 13 surface-water samples and in 2 of 3 replicate samples collected by the U.S. Geological Survey from 5 sites in the West Branch Canal Creek area from February through August 1999. The volatile organic compound concentrations ranged from below the detection limit to 22.1 micrograms per liter. Quality-assurance samples showed that the data were not measurably affected by contamination bias and that the variability of surface-water volatile organic compound analyses was higher than the variability of ground-water volatile organic compound analyses from previous sampling events. The higher variability in surface-water analyses compared to ground-water analyses was attributed to greater heterogeneity in concentrations of volatile organic compounds in surface water than in ground water.

The presence of volatile organic compounds in the creek raises concerns about the efficiency of natural attenuation to remove volatile organic compounds from ground water as it passes through the wetland sediments into the surface water. Extensive sampling of shallow ground water in the West Branch Canal Creek wetland study area by use of piezometers and porous-membrane sampling devices has shown that trichloroethylene and 1,1,2,2-tetrachloroethane readily degrade as contaminated ground water passes through the wetland sediments and that volatile organic compounds generally are not detected above their reporting limits in the ground water immediately below the surface (Lorah and others, 1997). Additional sampling of surface water and shallow ground water will be needed to determine whether the volatile organic compounds detected in the creek from February through August 1999 originated solely from cross-media transfer of contaminants from the ground water within the wetland study area, or whether additional sources of contamination exist upstream or downstream of the wetland study area that may discharge to the creek. Additional sampling and modeling may also be instrumental in determining whether the volatile organic compounds in the surface water originate primarily from localized near-surface “hot spots” or seeps that allow ground water to bypass the reducing wetland sediments, or from more widespread discharge of ground water from contaminant plumes.

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